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A MANUAL

OF

QUALITATIVE ANALYSIS.

BY THE SAME AUTHOR.

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I.—A KEY TO THE FIRST AND SECOND STEPS IN CHEMISTRY.

II.—A MANUAL OF TECHNICAL ANALYSIS.

A MANUAL

OF

QUALITATIVE ANALYSIS.

BY

ROBERT GALLOWAY, F.C.S.,

PROFESSOR OF PRACTICAL CHEMISTRY IN THE MUSEUM OF IRISH INDUSTRY.

FOURTH EDITION.

Revised and Enlarged.

LONDON:
JOHN CHURCHILL AND SONS, NEW BURLINGTON STREET

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PREFACE

TO THE

FOURTH EDITION.

In this Edition, I have divided the work into "Two Parts," the first part contains, with additions and alterations, the matter of the former Editions; the second part, which is introduced for the first time, is devoted to organic analysis.

The following are some of the chief alterations and additions in the first part:—Methods for detecting the impurities which the reagents may contain have been given. The photo-chemical methods of Merz as well as those of Cartmell and Bunsen have been described. The old method of separating cadmium from copper by means of carbonate of ammonia has been modified so as to render it more trustworthy. The alterations which have been made in the text on the separation of the groups will enable the student more readily to understand what to do with the several group precipitates, and how to treat the filtrates. Important alterations and additions have been made in the chapter on the Preliminary Examination of Solids.

In the second part the properties and reactions of the chief organic bodies of animal and vegetable origin have been given, including, of course, the chief members of the albuminoid, the gelatiginous, the saccharine or amylaceous, and the alkaline groups. Methods for the proximate analysis of urine and other animal matters, and the preparation and examination of the ash in organic substances have also been given.

The comparatively rapid sale of the former editions and the translation of the work into other languages have rendered the preparation of this edition an agreeable task, and I trust the additions and alterations which have been made in this Edition will be found to be improvements, and will therefore render the book still more acceptable to the student.

I have continued to employ the old nomenclature and notation, as very many students who have advanced in their chemical studies only as far as qualitative analysis are ignorant of the new notation and nomenclature, and therefore it would be very laborious and unsatisfactory for them to have to learn the new language of the science through the medium of a work on Qualitative Analysis: the language of chemistry ought to be taught in the same manner as all other languages. Students who know the new language know or ought to know the old, and therefore it will be no inconvenience to them to meet with the old, as they will understand it, and will be able, if necessary, to translate it into the new.

ROBERT GALLOWAY.

September, 1864.

PREFACE

TO THE

SECOND EDITION.

In issuing a New Edition of this Manual, I will here briefly describe the scheme or plan of analysis developed in the Work, and the way in which the book ought to be used.

In all other works on Qualitative Analysis with which I am acquainted, the properties of the bases and acids, and the application of these properties to the analysis of substances, are treated separately. As a consequence, the student, when he goes through the experiments on each base and acid, performs these illustrations of the properties without perceiving their use or application. In the part of the Work devoted to the analytical course, he is *told what to do* either by tables (as in the 'Giessen Outlines,' and some other works), or, as in Fresenius, by a more tedious and, in my opinion, as defective a method. The principles upon which these instructions are based are not given with the instructions, but in a separate chapter of the Work; and unless the student is able himself to unite the two—the principles with the practical instruction—he becomes a mere analytical machine. Students who can give their whole time and attention to the study of the science can, if they will, accomplish this; but I have found by experience, that those who can only devote some five or six hours in the week to the acquirement of the science fail to become intelligent analysts by this system.

The system is very difficult, as well as defective; it is so difficult, that those who employ it generally teach one thing, useless in itself, in order that they may teach another: they teach the student first to look for one acid and one base—a limitation which is not adopted in actual practice—solely for the purpose of rendering the course in which they have to look for all the bases and acids less difficult.

In the plan I have adopted, the properties of the different members of each group are contrasted by placing them in parallel columns; the advantage of this is, that the student, after he has performed the experiments, is able himself to devise methods for the detection and separation of the different members; it places him, in fact, in the position of a judge who has to decide some cause after having heard all the pleadings. It enables him also to judge for himself how many different methods might be adopted in the separation of substances; it therefore enlarges his views, and enables him to *reason* on the methods he adopts.

This Manual is intended to be used in the following way:—

The student commences with the first group; and after he has performed all the experiments given in the table of that group, several analyses are given him, each of which he examines for the members of this group. When he can perform these practical exercises correctly, he commences the second group—first performing the experiments in the group, and then analysing several solutions for the members of this group. When he can perform these correctly, he examines several solutions for the members of the first and second groups. In this progressive way he passes through the groups; so that by the time he has completed them, he will have become an accurate analyst.

In the former Edition I proposed, and partially carried out, the division of the third group of bases, by employing ammonia as a group reagent; this alteration not only simplifies the subject, but it makes the plan of analysis taught in the laboratory, more consonant with the methods adopted in actual practice. This alteration is fully carried out in this Edition, and a more complete description of the properties of the basic groups is given. I have also given, in this Edition, an outline of the special tests to be adopted in the detection of the acids, and considerable additions have been made in the Chapter on the Preliminary Examination of Solids. I have also introduced a new feature at the very commencement of the book; a series of experimental exercises are given, illustrating the principles upon which analytical operations are based, which it is intended the student should perform before he commences the groups. My aim in writing the book has been to furnish a suitable guide to the beginner; and I confidently hope that this Edition will be found superior to the former in this respect, and that it is what I wish it to be—a Student's Book.

R. G.

DUBLIN, *Nov.*, 1857.

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QUALITATIVE ANALYSIS.

PART I.

CHAPTER I.

INTRODUCTION — OPERATIONS — REAGENTS — APPARATUS — THE PRINCIPLES UPON WHICH ANALYTICAL OPERATIONS ARE FOUNDED— HOW THE WORK OUGHT TO BE STUDIED—SOURCES OF ERROR— SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS—ARRANGEMENT OF THE RESULTS OF THE ANALYSIS.

1. QUALITATIVE ANALYSIS enables one to discover the *composition* and *properties* of any unknown substance; and it teaches one the mode of *separating* substances from each other.

2. Only those substances which are commonly met with in nature, or which have some useful application, are treated of in this work; the following is a list of them:

3. BASES.—Potash, soda, ammonia, baryta, strontia, lime, magnesia, oxide of manganese, oxide of zinc, oxide of nickel, oxide of cobalt, the oxides of iron, sesquioxide of chromium, alumina, oxide of uranium, oxide of lead, oxide of silver, the oxides of mercury, oxide of bismuth, oxide of copper, oxide of cadmium, oxide of gold, oxide of platinum, oxide of antimony, the oxides of tin.

4. Inorganic Acids.—Arsenious acid, arsenic acid, chromic acid, carbonic acid, hydrosulphuric acid, hydrocyanic acid, sulphuric acid, boracic acid, phosphoric acid, oxalic acid, hydrofluoric acid, silicic acid, hydrochloric acid, hydrobromic acid, hydriodic acid, nitric acid, chloric acid.

5. Organic Acids.—Tartaric acid, citric acid, malic acid, benzoic acid, succinic acid, tannic acid, gallic acid, uric acid, acetic acid, formic acid.*

6. Each of these bases and acids is A SOLID, A LIQUID, OR A GAS; in whichever state it exists, it must be *soluble* or *insoluble* in water. If it is A SOLID, and *insoluble*, it will, on being separated from any of its soluble compounds, float in or upon the water or else fall to the bottom; in either case it is called a precipitate; if it is *soluble*, it will remain dissolved when separated from any of its soluble compounds. If it is a LIQUID, and *insoluble*, it will float upon the water if lighter than that liquid, and, if heavier, the water will float upon it; if it is *soluble*, it will mix with the water. If it is A GAS, and *insoluble*, it will, on being separated from any of its soluble or insoluble compounds, escape into the air; if it is *soluble*, it will remain dissolved in the water, if there is sufficient for its solution—if there is not sufficient, the *excess* will escape into the air; if it is dissolved by the water, it will most probably escape when the liquid is warmed, being expelled by the heat.

7. The bases, with the exception of ammonia, are all solid and non-volatile bodies. Potash, soda, ammonia, baryta, strontia, and lime, are soluble in water; the rest of the bases are insoluble in that liquid. The compound produced by the union of a base with an acid is called a salt. Many of the salts of the insoluble bases are soluble in water. The salts of the gaseous base, ammonia, and the salts of the gaseous acids, are solids; some of these solid salts are soluble, some are insoluble, in water.

8. If to a solution of any of the soluble salts of the insoluble

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* The behaviour of the more important animal and vegetable substances, such as starch, albumen, the organic alkaloids, &c., with reagents, is given in this edition, forming Part II.

bases a soluble base is added, the soluble base will take away the acid from the insoluble base; the latter—viz., the insoluble base—being set free, will consequently precipitate, on account of its insolubility in the liquid. We may here observe, that the bases, when they are set free in this manner, combine with water; this compound of the base and water is termed the hydrate of the base, whichever base it may be. The three following experiments are given to teach the student the principle just stated; he must, therefore, carefully perform the experiments according to the directions:

EXERCISES.

9. Dissolve, by the aid of heat, two or three grains of alum, which is a compound containing sulphate of alumina, in a test-tube half filled with water;* add ammonia to the solution after the alum is dissolved, and, after the addition, close the mouth of the test-tube with the thumb, and then shake the liquid in it very violently. If the liquid smells of ammonia *after the agitation*, a sufficient quantity has been added; but if it does not, a further quantity of ammonia must be added, and the liquid again shaken; and this must be repeated until *the liquid smells of ammonia after it has been well shaken*. The ammonia deprives the alumina of its acid; the alumina, on being set free, combines with water—this compound ($Al_2 O_3$, $3HO$),† appears under the form of a white, gelatinous solid, insoluble in water.

10. Dissolve two or three grains of sulphate of copper in a test-tube half filled with water; boil the solution, by means of a spirit or gas lamp, and add to the boiling liquid a solution of caustic soda, until it turns red litmus paper blue. After the caustic soda has been thoroughly mixed with it by agitation, in the way described in the first exercise (par. 9), oxide of copper (CuO), which is of a black colour, will precipitate, owing to

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* See "Solution," page 8.

† See "Precipitation," page 10.

its being deprived of the sulphuric acid by the soda. If the oxide of copper is precipitated under the boiling point, it combines with water, forming hydrate of the oxide (CuO, HO), which is of a blue colour.

11. Dissolve two or three grains of sulphate of zinc in a test-tube half filled with water; add ammonia, drop by drop, until a white precipitate, which is hydrate of zinc (ZnO,HO), is formed; then continue to add the ammonia until the precipitate disappears. The precipitate disappears, because the hydrate of zinc is soluble in ammonia; it is also soluble in the other alkalies, soda and potash; therefore, if caustic soda had been added, a precipitate would have formed, as in the case of the ammonia, which, on a further addition of soda, would have disappeared.

12. When substances are employed in analysis in the way ammonia and caustic soda have been employed in the above experiments they are called *tests*, or *reagents*, and the phenomena produced by them are termed *reactions*. The reagents are either acids, bases, or salts; and the reaction consists sometimes in a change of colour, sometimes in the production of effervescence, but most frequently by the formation of a precipitate, which, in many cases, possesses a characteristic colour. Reagents may be divided into two classes—*general* and *special*. The general reagents are employed to divide substances into *families* or *groups*, and the special reagents to detect the *individual members* of a group. A special reagent is said to be *characteristic*, when it produces a reaction so decisive that it admits of no mistake. A reagent is called *sensitive* or *delicate*, if its action is clearly perceptible with a very minute quantity of the substance tested for. The student must be very particular in always mixing thoroughly the reagent with the solution to which he has added it, and not simply content himself by adding it (as is generally the case with beginners), without attempting, by *agitation* to incorporate the two fluids. The way for incorporating them has been fully described in the first experiment (par. 9); it only remains for us to guard the student against the accident of losing the

liquid, which is likely to occur, when the liquid is hot, unless the operator keeps his thumb firmly fixed upon the mouth of the test-tube; because the air in the upper part of the test-tube, in passing over the heated liquid, becomes expanded, and would therefore expel the liquid, unless the mouth of the tube was kept firmly closed.

13. If to any salt of ammonia one of the soluble bases is added, the latter will deprive the ammonia of its acid; consequently, the ammonia will be set free, which will be perceived by the smell. The soluble bases set the ammonia free from its salts in the solid state, as well as in solution; heat assists the liberation in each case. If, to any salt of the volatile acids, an acid having a stronger affinity for the base of the salt is added, the volatile acid will be set free; the decomposition takes place as well when the salt of the volatile acid is insoluble as when it is soluble, in water. The following experiments illustrate the principles here stated.

EXERCISES.

14. Dissolve two or three grains of chloride of ammonium in a test-tube containing water; add to it some caustic soda solution, and then warm the liquid in the tube; ammonia will be set free in the gaseous state. It will be known, when it is in the *free state*, by the smell.

15. Mix two or three grains of dry, powdered chloride of ammonium very intimately with a like quantity of slaked lime; place the mixture in a crucible, and warm it by means of a spirit or gas lamp; ammonia will be set free as in the previous experiment.

16. Dissolve a few grains of carbonate of soda in water; add to the solution sulphuric, hydrochloric, or nitric acid—each of these acids deprives the carbonic acid of its base: it is consequently set free; and, by its escaping through the water into the atmosphere, causes an effervescence.

17. Place a few grains of chalk or marble at the bottom of

a test-tube; cover it with water, and then add to it hydrochloric or nitric acid—either of these acids deprives carbonic acid of its base, consequently it is set free; and by its evolution, produces effervescence, as in the previous experiment. Hydrochloric and nitric acids are to be preferred to sulphuric acid in this experiment, because the former give with lime, salts soluble in water; but the latter produces with that base, a salt, sulphate of lime, sparingly soluble in water; the greater part of the sulphate of lime therefore falls down, and thus shields the undecomposed chalk or marble from the acid.

18. The student will see by these two courses of experiments, that salts are decomposed by adding to them either acids or bases, provided the acids or bases added have stronger affinities than the acids or bases in the existing compound; and that, according as acids or bases are added, so acids or bases are set free. Thus, ammonia and alumina are liberated from their salts on the addition of a stronger base, and carbonic acid is liberated from its combinations on the addition of a stronger acid.

19. All the salts of ammonia containing volatile acids, on being heated volatilize completely, either with or without decomposition; but the ammonia salts of the non-volatile acids—viz., phosphoric, boracic, and silicic acids—are decomposed by heat; the ammonia escapes, but the non-volatile acid remains behind. The salts of the volatile acids do not volatilize, on being heated, unless ammonia is the base; the acid may be expelled by the heat, but the base with which it was combined remains behind, with the exception of ammonia. The following experiments are given to illustrate the principles here stated:

20. Place two or three grains of powdered chloride of ammonium in a crucible; heat the crucible, by means of a Berzelius spirit or gas lamp, until all fuming ceases.* The ignition must be continued so long, because the fumes are the volatilizing salt; and, therefore, until they cease, all the ammoniacal

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* See "Ignition" and "Sublimation," page 13.

salt is not expelled. If the chloride of ammonium employed is perfectly pure, there ought to be no residue after the fuming ceases.

21. Place two or three grains of powdered chalk in a crucible; heat the crucible for some time by means of a Berzelius spirit or gas lamp. After the lamp is removed, and the crucible has become cold, add some water to the ignited chalk, and then test the water with red litmus paper—it will change the colour of the paper from red to blue, showing that some of the carbonic acid has been expelled by the heat.

22. If, to the solution of any salt, an acid, or a salt containing an acid, is added, which acid would produce by combining with the base of the salt in solution, an *insoluble salt*, it will always take away that base from all other acids which form with that base soluble salts, and unite with it, producing the insoluble salt; also, if to the solution of any salt, a base, or a salt containing a base, is added, which base would produce by combining with the acid of the salt in solution an *insoluble salt*, it will always take away that acid from all other bases which form with that acid soluble salts, and unite with it, producing the *insoluble salt;* for in *whatever way* the most insoluble substances can be generated, decomposition occurs. The following experiments are given to illustrate the principles here stated:

EXERCISES.

23. Dissolve two or three grains of nitrate of baryta in a test-tube half filled with water; add to the solution a few drops of dilute sulphuric acid; the sulphuric acid will deprive the nitric acid of the baryta, by combining with that base, and forming with it an insoluble salt, sulphate of baryta.

24. Dissolve two or three grains of nitrate of baryta, as before; add to the solution a solution of sulphate of potash—sulphate of baryta and nitrate of potash will be produced. The

former, being insoluble in water, will be precipitated; the latter being soluble, will remain in solution.

25. Dissolve two or three grains of common salt, chloride of sodium, in water; add to the solution a few drops of nitrate of silver—chloride of silver and nitrate of soda will be produced. The former, being insoluble in water, will be precipitated; the latter, being soluble, will remain in solution.

26. Dissolve two or three grains of sulphate of potash in water; add to the solution some baryta water—sulphate of baryta will be formed, and potash set free. The former, being insoluble in water, will be precipitated; the latter, being soluble, will remain in solution.

27. Before attempting to show how these different principles are employed in analysis, we must describe the principal operations employed in analysis, and give a list of the reagents and apparatus required.*

OPERATIONS.

SOLUTION.

28. Many solid bodies, when placed in contact with a liquid, possess the property of becoming thoroughly incorporated with it, by passing into the fluid state. This change is expressed by the term *solution*, and the liquid in which the solid dissolves is called the *solvent*.

29. Solutions are of two kinds, *simple* and *chemical*. A *simple* or *mechanical solution* is the mere dissolving of a solid in a liquid, no chemical change occurring in either; on the removal, therefore, of the liquid by evaporation, the solid is obtained in its original condition. Common salt dissolved in water affords an illustration of a simple solution.

30. In a *chemical* solution the solid and fluid combine together, forming an entirely new substance, from which the

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* The student passes on to par. 96.

original solid and fluid can no longer be extracted by mere mechanical operations. Chalk dissolved in hydrochloric acid affords an example of a chemical solution.

31. The solvent in a simple solution cannot dissolve unlimited quantities of the substance to be dissolved; it can only dissolve certain fixed quantities of the solid, the amount varying with the kind of solid, and the amount of any particular solid varying with the solvent. When the solution contains as great a quantity of the solid matter as it is capable of dissolving, it is said to be *saturated.* A solution is known to be saturated when fresh solid matter of the same sort, on being put into it, remains undissolved. "But as fluids dissolve generally larger quantities of a substance the higher their temperature, the term *saturated,* as applied to simple solutions, is only relative, and refers invariably to a certain temperature." From the tendency of heat to diminish the force of cohesion, it naturally results that the solubility of most bodies is increased by heat; this, however, is not always the case; some bodies, as common salt, are equally soluble in water at all temperatures, whilst, in other cases, the solubility is greater at particular temperatures than either above or below them. The liquids employed as solvents in simple solutions are water, alcohol, ether, oils, &c. The most important solvent is water; the others are only resorted to when the substance to be dissolved is insoluble in that liquid.

32. "A chemical solution may be *accelerated* by elevation of temperature; and this is, indeed, usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference in temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature." The liquids which produce chemical solutions are, in most cases, either acids or alkalies.

33. The process of solution is conducted either in evaporating dishes or test-tubes. The latter are generally employed when

the quantity of the solid operated upon is small. The more minutely any substance is powdered, the more its solution is facilitated. Solid substances are generally reduced to powder in mortars.

PRECIPITATION.

34. It is frequently necessary to remove a constituent—it may be either the metal or metalloid of some binary compound, or the acid or base of some ternary one—from the liquid in which the compound is dissolved. This is effected by making it a constituent of some new compound, which is insoluble in the liquid in which the original compound was dissolved. This operation, which is called precipitation, is owing, therefore, to the formation of a new solid substance, which is insoluble in the liquid in which its elements were dissolved, and which falls, or is precipitated to the bottom, owing to the solid being specifically heavier than the liquid. Occasionally, however, it is lighter, and floats upon the surface. In both cases, the insoluble substance is called the *precipitate*, and the substance producing the precipitation is termed the *precipitant.*

35. Precipitation is an operation which is constantly practised in the preparation of substances in the manufactory as well as in the laboratory. We also resort to it in the laboratory for the purposes of detecting and separating substances one from another. Thus, if we had a solution which might contain some compound of baryta and lime: to ascertain whether baryta was present, and, if it was, to separate it from the solution, before ascertaining whether lime was likewise present, we might add a soluble chromate—if baryta was present, the chromic acid would combine with it; and as chromate of baryta is insoluble in water, it would precipitate, whilst chromate of lime, being soluble, would remain in solution. If we were now to add to the clear, filtered solution some soluble oxalate, oxalate of lime, being insoluble in water, would precipitate. If the chromate produced no precipitate, there

could be no baryta; if the oxalate produced no precipitate, after having separated the baryta (if present), lime must be absent.

36. Precipitates are classified, according to their appearances, into *crystalline*, *pulverulent*, *flocculent*, *curdy*, and *gelatinous*. The terms *turbid* and *turbidity* are applied when the precipitate is so small that it cannot be distinguished, except by impairing the transparency of the fluid.

37. The separation of precipitates from liquids is, with some few exceptional cases, much assisted by the application of heat and agitation. The operation, when performed as an analytical operation, is conducted in test-tubes, which, from their transparency, admit of an inspection of the process.

FILTRATION AND DECANTATION.

38. These terms are applied to a modification of the same operation—viz., the mechanical separation of fluids from solid matter mixed with them.

FILTRATION.

39. In filtration, the separation of the fluid from the solid matter is accomplished by passing it through filtering paper of a proper size and shape, supported in a funnel. The pores of the paper permit the fluid to pass through; whilst the solid matter, being prevented, remains behind.

40. To prepare a filter, take a small piece of filtering paper (the best white blotting paper), and fold it twice, from side to side; then round off with scissors the projecting corners, so that the paper may fall wholly within the funnel; moisten the paper when placed within the funnel, and then carefully pour the liquid to be filtered upon it. The funnel, when large quantities have to be filtered, is supported in one of the rings of the retort stand; but in the ordinary filtrations required in qualitative analysis, it may rest on the mouth of a test-tube.

The filter should not project over the edge of the funnel, especially if the substance in the filter requires to be washed. Should the first portions of the liquid which pass through the filter not be perfectly bright, which is frequently the case, they must be returned to the filter, and this must be repeated until it is perfectly bright. The liquid which passes through the filter is called the *filtrate*.

DECANTATION.

41. When the solid particles are very heavy, the supernatant liquid can be perfectly separated, without passing it through a filter, by simply inclining the vessel, so as to allow the fluid to pass away unattended by the precipitate, or by removing the fluid by a syphon.

42. The separation in this way of a solid from a fluid is called *decantation*.

43. Too great attention cannot be paid to the washing of precipitates when they are required for further examination. After the precipitate has been thrown upon the filter, a stream of water must be projected from the wash-bottle upon it, from time to time, until it is perfectly freed from *soluble matter;* this is soon accomplished if hot water be employed. Hot water may therefore be used in all cases unless the contrary be expressly stated.

EVAPORATION.

44. This process is used for the purpose of obtaining matter in a solid state from solutions. By the aid of heat, the volatile fluid passes off in the gaseous form, whilst the non-volatile matter remains behind.

45. If the evaporation be conducted slowly, the solid matter will frequently, on being deposited, assume a crystalline form. The operation is then termed *crystallization*.

46. This operation is frequently conducted for the purpose

of obtaining a liquid in a more concentrated form, by volatilizing a portion only of the fluid. Vessels are constructed expressly for the purpose called evaporating dishes.

DISTILLATION.

47. This operation, like the former one, consists in the separation of a *volatile* from a *less volatile* fluid, or in the separation of a *liquid* from a *solid.* But in evaporation no attention is paid to the volatilized fluid, whilst in distillation it is frequently the only substance required. A distilling apparatus is therefore so constructed as to allow the evaporated fluid to be collected, which is called the *distillate.* It consists of three parts:—1. A vessel in which the liquid to be distilled is heated. 2. An apparatus in which the vapour is cooled and condensed. 3. A vessel for receiving the distillate.

48. On a small scale, glass retorts are employed; but in the distillation of large quantities, copper stills are usually substituted for them.

IGNITION.

49. By this operation volatile is separated from non-volatile solid matter; it requires the application of a high temperature, and must be conducted in crucibles. This process is therefore an *evaporation of solid bodies.*

SUBLIMATION.

50. By sublimation we effect not only the separation of volatile from less volatile solid matter, but by cooling we bring the volatile matter back to the solid state, and in this state it is called the *sublimate.*

51. This process is therefore a *distillation of solid bodies.*

FUSION.

52. This term is applied to the liquefaction of a solid, by the mere application of heat. It is also used for the decomposition of solids in the "dry way."

53. By this operation we are able to resolve insoluble substances into forms which admit of solution. This is accomplished by causing their proximate elements to unite with bodies the compounds of which will be capable of solution. Thus sulphate of baryta, which, from its insolubility both in water and acids, resists the action of reagents in the fluid state, is decomposed in this way. It is mixed with three or four times its own weight of dry carbonate of soda, and the mixed mass exposed in a crucible for some time to a high temperature. The two salts mutually suffer decomposition when placed in these conditions, the sulphuric acid passing over to the soda whilst the carbonic acid unites with the baryta. If the fused mass be treated with water, the sulphate of soda dissolves in that liquid, whilst the carbonate of baryta, being insoluble, remains behind. This substance, after being well washed, may be dissolved in hydrochloric or nitric acid. The decomposition of substances in the dry way requires, in most cases, a higher temperature than that which a small spirit lamp affords. When a limited amount of heat can only be obtained, it is better to employ a mixture of equal parts of carbonate of soda and carbonate of potash, instead of the former salt alone.

DEFLAGRATION.

54. This term is applied to all decompositions attended with noise. It also includes the oxidation of a substance by a reagent, in the dry way, on account of the slight explosions which frequently attend this kind of oxidation.

THE BLOWPIPE.

55. The mouth blowpipe is a small instrument which is employed for directing a fine and continuous stream of air into the flame of a candle or lamp. By the flame thus produced two reverse chemical operations may be performed, viz., *oxidation* and *reduction*. The flame is therefore distinguished by these properties into the outer or *oxidizing* flame and the inner or *reducing* flame.

56. In the *oxidizing* flame, the inflammable vapour is in a state of complete combustion, being supplied and mixed with an excess of atmospheric air. From the high temperature resulting from the perfect combustion of the imflammable vapour, and likewise from the excess of oxygen, all the requisite conditions are present for causing substances with an affinity for that element to enter into union with it.

57. In the *reducing* or *deoxidizing* flame the inflammable vapour is in an incomplete state of combustion, due to a deficiency of atmospheric air; hence any metallic oxide placed in this portion of the flame is robbed of its oxygen by the inflammable vapour, which requires that element for its combustion.

58. A *reducing flame is obtained* by keeping the nozzle of the blowpipe in an inclined direction, parallel to the surface of the wick, and just touching the exterior surface of the flame. An *oxidizing flame is obtained* by keeping the nozzle of the blowpipe at the same inclination as in the former case, and introducing it into the flame to about one third the breadth of the wick, at such a distance only from the surface of the latter as to obtain a clear, unbroken flame. A weak blast of air is only required for the reducing flame, but a strong blast is required for the oxidizing flame.

59. The *colour* of the reducing flame is *bright yellow* if an oil lamp or candle is used; but if gas is used, it should be of the same blue colour as the centre of the oxidizing flame. The

colour of the oxidizing flame in all cases is a pale-blue, almost invisible by daylight.

60. "When any substance is submitted to the action of the *reducing flame*, it should be so held as to be entirely surrounded by the reducing flame, and protected from the oxidizing action of the surrounding atmosphere; but this condition being fulfilled, it should be held as near as possible to the point of the flame, in order to gain the greatest amount of heat and prevent any deposition of soot, which would shield the substance from the action of the flame, and would be occasionally attended with other disadvantages."

61. When a substance is submitted to the action of the *oxidizing flame*, it should be held just beyond the point of this flame if a candle or oil lamp is used; but if gas is used, it should be held at a considerable distance (viz., one half to three quarters of an inch) beyond the point of the visible flame.

62. "As the current of air which is supplied ought to be continuous, its production requires some attention and address. The air is not blown directly from the lungs, but is forced from the mouth by means of the cheeks. The difficulty consists in inspiring and expiring through the nose, while a continued stream escapes from the mouth. This may be attained by attention to the following directions:—Inflate the mouth fully, and then, with the lips firmly closed, and the back of the mouth closed by the tongue, breathe freely through the nostrils. While the respiration proceeds, and the mouth is inflated, allow a little air to escape through a very minute opening between the lips, renewing the supply in the mouth by occasionally admitting air from the lungs without interfering with the process of respiration through the nose."—*Parnell.* In attempting this, the student will not, probably, be immediately successful, but a few days' persevering practice will enable him entirely to master this primary difficulty.

63. *The flame of the blowpipe.*—When coal-gas is available, it is to be preferred, since it is perfectly free from dirt and

grease, and admits of being regulated with the greatest nicety. The gasburner ought to be of an oblong shape instead of round, the current of air being blown lengthways. When gas cannot be procured, an oil lamp or wax candle may be used. An oil lamp proper for blowpipe operations can be obtained at any of the shops where they sell chemical apparatus—it need not, therefore, be described; it will be sufficient to say that it must have a broad and moderately thick wick, and that on each occasion the wick must be trimmed* before employing the flame for the blow-pipe experiments. The best kind of oil for the lamp is pure rape or olive oil. The flame of a wax candle is far inferior in size and intensity to that of a lamp.

64. *Description of Bunsen's lamp.*—The lamp invented by Bunsen, in which gas is burned without luminous or fuligenous flame, can be used to produce all the reactions for which the blowpipe is usually employed, and with greater ease and certainty. In many cases reactions can be obtained, and even the approximative quantity of substances determined, which, with the ordinary blowpipe, are either impossible, or can only be effected by difficult and tedious processes.

65. Fig. 1 represents the blowpipe lamp. A conical iron-plate chimney, 30 millimetres wide at the top, and 55 millimetres at the bottom, is so fixed on the supports *a a a*, that the burner tube *b* is in the axis of the chimney, and terminates 45 millimetres below the upper aperture. By this arrangement the flame has the form represented in the vertical section fig. 2; *a b a* corresponds to the dark part of the ordinary luminous flame, and contains the unburned gas mixed with air. If the gas cock is so adjusted that the point *b* is exactly level with the upper aperture, a flame is obtained of unvarying dimensions, which remains quite steady, and is sharply defined in all its parts, and which will always have the same uniform character. *a d a b* is the burning cone of the flame, and is so little luminous as to be scarcely perceptible. In this cone the external mantle *a d a c* may be distinguished from the internal

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* The wick must be evenly cut, and perfectly free from all extraneous fibres.

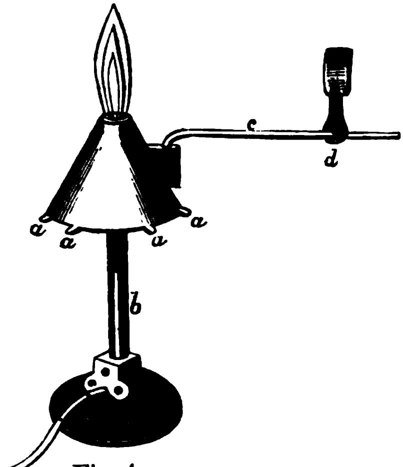

Fig. 1.

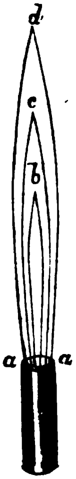

Fig. 2.

mantle *a c a b*, by being of a more intense blue. The holder, fig. 3, serves to hold the test specimens, which must not be

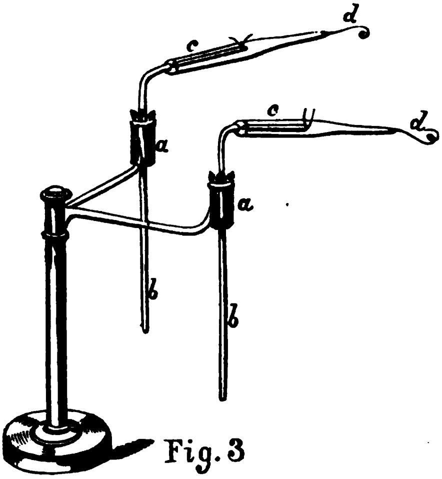

Fig. 3

larger than a millet grain, and to expose them to the action of the flame. In the two tubes *a a*, which are lined with cloth, two glass rods *b b*, bent at right angles, move easily in any direction. On the end of the rods are two glass tubes *b*, drawn out to solid ends; in these are fused platinum wires, about 0·145 millimetres thick, bent at their extremities to fine loops. To allow these glass tubes to be firmly fixed to the glass rods, and yet allow them at the same time of being easily and gently pushed in and out, a silken thread, provided with a knot, is drawn through the whole length of the tube; this silken thread acts as a spring, and causes the tubes to glide easily. To bring about this, an aperture is made in the sides of the tubes through which the thread is carried.

66. If the loop of the platinum wire when moistened is slightly brought into contact with the powder or the grain of the substance to be examined, it adheres to it, and when some time warmed near the flame, and then introduced into it, the substance melts or fuses into a drop or bead. Spluttering substances must first of all be brought to a red heat in a covered platinum spoon. By means of the holder fig. 3, the substance under examination can thus be brought to any part of the flame required.

67. The temperature of the flame depends mostly on the composition of the gas; it will be found that the hottest part of the flame is in a zone of the external mantle *a d a c*, which extends a few millimetres above and below the diameter of the flame at *b*. This region which may be called the *melting space* or *zone of fusion*, is used to determine the deportment of bodies at the temperature of 2300° C. The external edge, of this melting space acts as an *oxidizing* flame, and the internal as a *reducing* flame. The latter is most powerful just below the point *b*.

68. The great constancy of the flame permits it to be used for determining the volatility of bodies at 2300° C. This is effected by melting on the platinum wire as much of the substance to be tested as will form, when seen under the microscope, a bead of 1 millimetre in diameter; with a little prac-

tice this is very easy. After the bead has been brought to the right size, and warmed by being brought near the flame, it can, by a very slight movement of the arms of the holder (fig. 3), be introduced into the melting-space of the flame, and the seconds which elapse until it has quite evaporated, are counted by means of a pendulum or metronome. This point is generally so marked by a sudden alteration of the flame as to be determinable to half a second.

69. Taking the volatility of carbonate of soda as unity, we may compare with it the volatility of equal bulks of other substances. If t_0 be the time required for the evaporation of carbonate of soda, and t_1, t_2, t_3, &c., that required for the evaporation of other substances we obtain the values $\frac{t_0}{t_1}, \frac{t_0}{t_2}, \frac{t_0}{t_3}$, &c., as approximate measures for their volatility.

70. The following determinations of volatility will illustrate the use to which they may be applied in geological chemistry, more especially if the balance be used, as is necessary in very accurate determinations.

Sulphate of soda	0·77
Sulphate of lithia	0·89
Sulphate of potash	1·21
Carbonate of soda	1·00
Carbonate of lithia	1·70
Carbonate of potash	2·30
Chloride of sodium	6·57
Chloride of lithium	8·36
Chloride of potassium	15·33
Boracic acid	0·84
Borate of soda	1·02
Phosphoric acid	23·00
Bibasic phosphate of soda	0·12

71. All these substances are easily and completely volatile at 2300° C. Other substances under the same circumstances lose only a single constituent, and leave a non-volatile residue. For instance, the sulphates of lime, strontia, and baryta lose

some of their SO_3, and become alkaline; the same is the case with the chlorides of calcium, strontium, and barium, and many other chlorides; they are converted in an analogous manner into basic compounds. The silicates rich in alkalies lose considerable quantities of potash and soda at 2300° C., at a temperature, therefore, much less than that of many lava streams.

72. Besides these determinations of volatility, the flame can be used for many valuable blowpipe experiments, among which is the quantitative determination of soda in the presence of lithia and potash.*

73. SUPPORTS.—Various materials are used as supports for substances during the time they are exposed to the blowpipe flame; the principal are charcoal, platinum wire and foil, and glass tubes. The kind of support is regulated by the change we wish to effect upon the substance under examination.

74. Charcoal.—The properties which make charcoal so valuable as a material for supports in blowpipe experiments are—1st, its infusibility; 2nd, its low conducting power for heat, which permits substances being heated more strongly upon a charcoal than upon any other kind of support; 3rd, its porosity, which makes it imbibe readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on the surface; 4th, its power of reducing oxides, which greatly contributes to effecting the reduction of oxides in the inner blowpipe flame.

75. Charcoal supports are used principally in the reduction of metallic oxides, &c., or in trying the fusibility of bodies. The substance to be subjected to the blowpipe flame—which, if in powder, should be previously moistened with a little water to make it cohere—is placed in a shallow hole made in the charcoal either with a knife or with a proper charcoal borer, and the charcoal is so held that the flame may impinge upon it at an angle of about 20 degrees. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the

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* The method for performing the quantitative determinations is given in the Appendix to Part I.

outer flame the metallic fumes are reoxidized, and the oxide formed is deposited around the portion of the matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colours leading to the detection of the metals.

76. Charcoal made from light woods—as the alder and pine—is the best for blowpipe experiments. It must be well-burned; it must be compact and free from crevices; it must not scintillate, smoke, or burn with flame; and it must of course, be perfectly dry. It should be cut by a small-toothed saw into pieces about six inches in length and from one to two inches in breadth, having a flat smooth surface at right angles to the rings of growth. It is this surface which is always to be used; and a good piece of charcoal may be made to serve for repeated experiments by simply filing off the used surface, and exposing a new one after each operation. As it is very difficult to get charcoal sufficiently good for blowpipe experiments, Mr. John J. Griffin, has provided an excellent substitute, an account of which is given in pars. 81 to 87.

77. *Platinum.* Platinum wire, and occasionally platinum foil, is used in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them and to watch the phenomena attending the solution and mark the colour of the bead; lastly, also to introduce substances into the flame, to see whether they will colour it.

78. The ends of the wire are twisted into a small loop (Fig. 4), and when required for use, the loop is moistened with a drop of water, then dipped into the powdered flux (when a flux is used), the portion adhering to the wire is then exposed to the flame of a gas or spirit-lamp, when fused, and whilst still hot, it is dipped again into the powdered flux, and this is continued until the loop is completely filled with the

FIG. 4.

flux after it has been fused. The bead when cold is moistened again, and a small portion of the substance to be examined put on and made to adhere to it by the action of a gentle heat. The loop is then finally exposed, according to circumstances, to the inner or to the outer blowpipe flame.

79. A great many metallic oxides dissolve in borax, forming coloured glasses. If any metallic arsenides or sulphides are present in the substance which has to be examined with borax, the substance must be roasted by the method described in the next par. (80) before making the examination with borax; and it is frequently advantageous, before roasting the powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

80. *Glass Tubes.* Tubes of hard German glass of about a quarter of an inch internal diameter, five or six inches long and open at both ends, are used in blowpipe experiments principally for roasting substances containing sulphur, arsenic, selenium, antimony, tellurium, &c., which, when heated with access of air, evolve fumes which may be recognised by colour, odour and chemical reaction.

81. *Small Glass Bulbs,* or what answers equally well, glass tubes closed at one end of about two and a half to three inches long, and from one eighth to one fourth of an inch internal diameter, are employed to test substances for water, mercury, sulphur, or other bodies which are volatilized by the application of heat without the access of air. The volatile products collect in the neck of the bulb or tube and may be judged of by their colour, odour, &c.

82. *Griffin's substitute for charcoal.* "The blowpipe experiments that require the assistance of charcoal may be divided into two classes. In the first class may be named the formation of beads with microcosmic salt, the trial of fusibility *per se*, and the roasting of the metallic compounds that contain such volatile elements as sulphur and arsenic. The second class of experiments is restricted to the fusion of minerals or metallic compounds with carbonate of soda, or with soda and borax, for the purpose of effecting particular combina-

tions, or of procuring their metals in a state of regulus. For these two classes of experiments I make use of two different composition supports, the first of which I call *Supports for Fusions*, and the second, *Supports for Reductions*. They are alike in appearance. Each consists of two parts—an upper or combustible portion, and a base or incombustible portion. The former is the proper substitute for the ordinary charcoal, the under portion acting only as a crucible, in which the combustible portion is contained. I shall first describe the composition and formation of the supports, and afterwards show the way to use them.

83. "The incombustible portion of both supports is made of fine pipeclay and charcoal powder, mixed in equal parts by weight with as much water, slightly thickened with rice paste, as is sufficient to form a stiff plastic mass.

84. "The combustible portion of the *Support for Fusions* consists of—

Charcoal, in fine powder .	12 parts.
Rice flour	½ "
Water, about . . .	8 "

The rice is boiled in the water to form a paste, with which the charcoal is afterwards mixed into a mass of the consistence of dough.

85. "The upper part of the *Support for Reductions* consists of the following mixture:—

Charcoal, in fine powder .	9 parts.
Carbonate of soda, crystallized	2 "
Borax, crystallized . . .	1 ,
Rice flour	½ "
Water, about	8 "

The water is boiled, the soda and borax are dissolved in it, and the rice is then added to form a paste, with which the charcoal is finally incorporated, and the whole well kneaded into a stiff mass. The mould in which these compositions are pressed to form the supports is made of boxwood.*

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* These moulds, and every other part of the apparatus, are sold by

86. "The principal points which require attention to ensure success in this process are to have the materials in the state of a very fine powder, and the moist compositions of a proper degree of consistency. If they are too soft, the support will not quit the mould without losing its form; if too dry, the particles of the support will not cohere. The proper state is found after a few trials. It is most convenient to begin by making the mixture too soft, and then drying it slowly till it is found to be hard enough to work easily. The composition is rolled into balls with the fingers. The moulds should be kept clean, and the forming parts of the pestle for the charcoal composition, and the ring, should be oiled. The point of the pestle for the clay composition must not be oiled, because grease prevents the adhesion of the combustible portion of the clay base. A pestle made on purpose for the operation, is used to remove the finished support from the mould, by pressure on the clay foundation.

"When the support is taken from the mould, it is placed on a hot plate or sand-bath to dry, after which the rough edges are taken off by a rasp. It is then ready for use. The bottoms of *supports for reductions* are painted with red ochre, mixed with rice paste, to distinguish these from the other kind. The size I have fixed upon is as follows:—height, half an inch; diameter at top, half an inch; at bottom, two fifths of an inch. The weight is about 16 grains, consisting of 10 grains of clay crucible, and 6 grains of combustible matter. I have tried several other sizes, but this I find to be the most generally convenient. Nevertheless, a higher temperature can be produced upon a smaller support; and I find that large masses of charcoal are not essential, since many blowpipe experiments can be finished during the combustion of only two grains of charcoal. When in use, they are supported by a handle made of wire, turned into the form of a ring: a piece of tobacco pipe can be used for the handle of the wire support.

87. "The following is the method of using these supports:

Mr. Griffin, and, I have no doubt, can be procured through any of the other dealers in chemical apparatus.

"Firstly, the surface of one of the supports for fusion is heated before the blowpipe flame. The support continues to burn like an ordinary pastile, till it is consumed down to the clay: in this respect the support has a superiority over common charcoal, which soon ceases to burn when removed from the fire. The ignited support is then to be rested upon a porcelain capsule, and a quantity of microcosmic salt, sufficient to form a bead, is placed on its red-hot surface. The salt instantly melts, and sinks into the central cavity, so as to form a bead; the heat, the form, and the smoothness of the surface of the support, facilitating this part of the process. The salt is then heated before the blowpipe, till it is converted into a transparent, colourless bead. The support is again placed on the porcelain capsule, and the metallic substance intended to be incorporated with the bead is added to it. The support continuing to be red-hot, and the bead consequently continuing soft, the substance so added is immediately absorbed, and its loss by dispersion prevented; whereas, upon common charcoal the fused salt solidifies soon after it is removed from the flame: and the substance added for examination, not adhering to it, is often blown away by the first blast from the blowpipe jet. The bead is now again fused, till the substance added to it is decomposed, and the resulting glass is observed to fuse quietly. It is then ready for examination; but it is sunk in the bottom of the hollow of the support, and cannot be seen by transmitted light, unless the projecting sides of the support be removed. This is effected as follows: the support is placed, as before, on the porcelain capsule, and the operator blows with his mouth, without the blowpipe, strongly down upon its surface. The pastile then burns away rapidly, and the force of the blast disperses the ashes, until the whole rim of the support is consumed. The bead then appears situated on the summit of a cone, and can be examined either by reflected or transmitted light. It is also in a position adapted for exposure to the different action of the oxidating and reducing flames, so as to have the character of the included metal fully developed. If, finally, the charcoal is allowed to burn wholly away, the coloured bead can be lifted from the ashes and preserved in a glass tube for subsequent examination and comparison.

"Secondly, if the surface of one of the *supports for reductions* be heated before the blowpipe, it becomes at first like the simple charcoal support; but in proportion as the charcoal is consumed, the fluxes which were mixed with it, and which are not volatile, concentrate and fuse upon the surface of the residue. If, therefore, a reducible metallic compound is heated upon such a support, it becomes at once exposed to the reducing action of the high temperature, of the nascent oxide of carbon, and of the carbonate of soda, whilst any earthy matter that it may contain is vitrified by the attendant borax."—*Griffin.*

APPARATUS REQUIRED IN PHOTO-CHEMICAL EXPERIMENTS.

88. A large number of substances are volatilized when a small particle of the substance in the solid state is introduced into the inner flame of a gas or spirit-lamp. Many of these substances in volatilizing colour the outer flame, and as the colour imparted to the flame is in most cases different and distinct for each substance, the coloration of the flame has long been employed in chemical analysis as a test for many substances. Thus—Soda and its salts impart to the flame a yellow, potash and its salts a violet, strontia and its salts a crimson colour. The intensity of the colour of the salts of the same base, varies with their volatility, the most volatile of the salts producing the most intense coloration. Difficultly volatile salts produce only a slight, and non-volatile salts no coloration; thus, with silicates and other non-volatile compounds, such as are met with in nature, it is often difficult to detect 3 or 4 per cent. of the alkalies. In such cases the coloration may frequently be produced by adding some other substance which has the power of decomposing the compound under examination, and forming, with the substance we wish to detect, a compound which will volatilize at the temperature of the flame. If we add, for instance, to silicates containing only 3 or 4 per cent. of the alkalies, a little *pure* gypsum, this will decompose

the silicate, a volatile alkaline sulphate, which will impart a colour to the flame, being formed.

89. As the colour produced by one substance interferes or entirely obscures that produced by another, we were formerly unable to detect more than one body in a mixture of substances by means of the colour imparted to the flame. This defect has lately been overcome by looking at the coloured flame through coloured media, as coloured glasses and coloured liquids, which intercept the colour produced by one substance, whilst they allow the colour produced by another substance to pass. Thus, the yellow colour produced by sodium compounds obscures the violet produced by potassium ones; Cartmell, who was the first to employ coloured media, proposed, in order to detect potash in the presence of soda by means of the coloured flame, to view the flame through a blue glass stained with cobalt: through this coloured glass no coloured rays from soda (or lithia) can pass, but it admits those peculiar to potash.

90. A solution of indigo can also be employed for the same purpose, Cartmell, for instance, detected lithia in the presence of soda and potash, by comparing the mixed colour of the flames of those bases with that of the flame of pure potash, when both are viewed through an indigo solution. Bunsen has found that the discrimination of these bases in presence of each other is more easily effected by observing the *succession of changes of colour*, which the mixed flame produced by these substances experiences when the rays reach the eye after passing through gradually thicker layers of an indigo solution. For this purpose a hollow plate glass prism (fig. 5) is used,

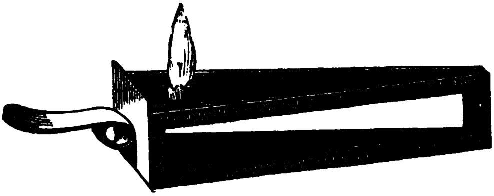

Fig. 5.

filled with indigo solution; it is 40 millimetres high, and its principal section is a triangle, with two sides of 150 millimetres, and the other of 35 millimetres. The indigo solution is made by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, diluting with 1500 to 2000 parts of water, and filtering.

91. In the following experiments the prism was moved horizontally before the eye, so that the rays of the flame always passed through gradually thicker layers of the medium. The alkaline substances, brought singly into the melting-space, exhibited the following changes:—

1. *Chemically pure chloride of calcium* produces a yellow flame, which, even with very thin layers of the indigo solution, passed through a tinge of violet into the original blue lamp flame.

2. *Chemically pure chloride of sodium*, the same.

3. *Chemically pure carbonate or chloride of potassium* appears of a sky blue, then violet, and at last of an intense crimson red, even when seen through the thickest layers of solution. Admixtures of soda or lime do not hinder the reaction.

4. *Chemically pure carbonate or chloride of lithium* gives a carmine-red flame, which, with increasing thickness of the medium, becomes gradually feebler, and disappears before the thickest layers pass before the eye. Lime and soda are also without influence on this reaction.

92. Merz has proposed, employing, in addition to the cobalt blue glass, a *violet*, a *red*, and a *green* glass; the violet glass is tinted with sesquioxide of manganese; the red glass (partly coloured and partly uncoloured) with sub-oxide of copper; and the green glass with sesquioxide of iron, and protoxide of copper. The common coloured window glass will generally be found to answer the purpose.

REAGENTS.

93.—LIST OF THE REAGENTS EMPLOYED IN THE FLUID STATE.

1. *Hydrochloric acid* (muriatic acid), if *pure*, is perfectly colourless, and leaves no residue when evaporated. The substances with which it is generally contaminated are iron, arsenic, and sulphuric acid. It may also contain chlorine and sulphurous acid.

If it gives, after dilution with distilled water, a precipitate with chloride of barium, sulphuric acid is present. If it turns yellow on evaporation, or if, after adding ammonia in excess, then acidifying with acetic acid, it gives a blue colour after the addition of a solution of ferrocyanide of potassium, it contains peroxide of iron. If it imparts a blue tint to a solution of iodide of potassium mixed with starch paste, it contains chlorine, and if it discolours a fluid made faintly blue with iodide of starch, it contains sulphurous acid. Examine it for arsenic by Marsh's test, described in the fifth group of bases.

Dilute one part of the concentrated acid with four parts of water.

2. *Nitric acid* (aqua fortis), when free from non-volatile matter, leaves no residue on evaporation. The impurities often found in it are hydrochloric and sulphuric acids.

If, after dilution with distilled water, it gives a precipitate with chloride of barium, sulphuric acid is present; and if the diluted acid gives a precipitate with nitrate of silver, chlorine is present.

Dilute one part of the concentrated acid with five of water.

3. *Nitro-hydrochloric acid* (aqua regia) is prepared by adding four parts of concentrated hydrochloric acid to one of concentrated nitric acid.

"Nitric acid and hydrochloric acid decompose each other, the decomposition, mostly resulting, as *Gay Lussac* has shown, in the formation of two compounds which are gaseous at the ordinary temperature, NO_2Cl_2 and NO_2Cl, and of free chlorine and water. If one equivalent of NO_5 is used to three equivalents of HCl, it may be assumed that only chlorohyponitric acid ($NO_2\ Cl_2$), chlorine and water are formed ($NO_5+3HCl=NO_2Cl_2+Cl+3HO$). This decomposition ceases as soon as the fluid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the free chlorine, and also, but in a very subordinate degree, that of the acids named, makes aqua regia our most powerful solvent for the metals (with the exception of those which form insoluble compounds with chlorine)."

This test is employed in an undiluted state.

4. *Sulphuric acid* (oil of vitrol) frequently contains arsenic, oxide of lead, sesquioxide of iron, lime, and oxides of nitrogen. The lead is deposited to a great extent when the acid is diluted, sulphate of lead being less soluble in dilute than in concentrated sulphuric acid.

This acid ought to leave no residue upon evaporation on platinum; and if it does not remain perfectly clear upon dilution with four or five parts of spirits of wine, oxide of lead, sesquioxide of iron, or lime is present. "The presence of small quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test tube; if the point of contact is marked by turbidity (chloride of lead), lead is present." If a solution of proto-sulphate of iron is poured upon some of the acid in a test tube, so that the iron solution floats upon the acid, a purplish red ring will be formed at the junction of the two solutions, if the acid contains nitric or hyponitric acid. If, after dilution with 20 parts of water, it imparts a blue tint to a solution of iodide of potassium, mixed with starch paste, hyponitric acid is present. Examine it for arsenic by Marsh's test, described in the fifth group of bases.

The dilute acid is prepared by adding four parts of water to every one of the concentrated acid.

5. *Tartaric acid* is generally sufficiently pure for analytical purposes. As it undergoes decomposition in solution, a small quantity only should be prepared at a time.

For use, dissolve one part, by weight, of acid, in two parts, by measure, of water.

6. *Bitartrate of soda* is prepared by dissolving a quantity of tartaric acid in water, dividing the solution into two equal parts, and neutralizing one exactly with carbonate of soda, and then adding the other portion, and afterwards evaporating the whole solution until the bitartrate crystallizes.

For use, make a saturated solution.

7. *Acetic acid*, when employed in analysis, ought to leave no residue on evaporation, and after saturation with carbonate of soda, emit no empyreumatic odour. It ought to give no precipitate with chloride of barium and nitrate of silver, and it ought to give no colour or turbidness with hydrosulphuric acid, or with sulphide of ammonium, after it has been neutralized with ammonia.

The ordinary commercial acetic acid is sufficiently concentrated for analytical purposes.

8. *Hydrosulphuric acid* (sulphuretted hydrogen) is prepared by adding to sulphide of iron, in an appropriate apparatus, dilute sulphuric or hydrochloric acid. The sulphuretted hydrogen is liberated in its gaseous state, and may be passed through any solution under examination; or a solution of the gas may be obtained by passing it through pure water. As this solution very soon decomposes by contact with the atmosphere, it ought to be prepared very frequently, and kept in well-stoppered bottles.

Sulphide of iron, from which hydrosulphuric acid is obtained, is prepared by projecting a mixture of thirty parts of iron filings with twenty-one of flowers of sulphur, in small portions at a time, into a red-hot crucible, replacing the cover after each addition. When the whole has been added, the ignition must be continued for a short time, until the excess of sulphur has been dissipated.

9. *Sulphurous acid* is prepared by acting upon copper or charcoal with sulphuric acid. For this purpose small pieces of charcoal are introduced into a flask, with from six to eight times their weight of sulphuric acid, and a moderate heat ap-

plied. The evolved gas must be conducted into cold water until it is no longer absorbed. On account of the great tendency which this reagent has to absorb more oxygen, and become converted into sulphuric acid, it must be preserved in well-stoppered bottles.

10. *Chlorine gas* is prepared by introducing into a flask one part of peroxide of manganese along with four parts of hydrochloric acid; the liberation of the chlorine is assisted by a gentle heat. A solution of the gas may be prepared by passing it into cold water. Chlorine water must be kept in well-stoppered bottles, and excluded from the light.

11. *Oxalic acid.*—Dissolve one part, by weight, of the acid, in twenty parts, by measure, of water.

12. *Oxalate of ammonia* ought to leave no residue after ignition on platinum foil, and it ought not to give a precipitate, nor be rendered turbid, by hydrosulphuric acid, nor by sulphide of ammonium.

Dissolve one part, by weight, of the salt, in twenty parts, by measure, of water.

13. *Ammonia* must be colourless, and leave no residue upon evaporation to dryness. It ought not, after being diluted with three volumes of distilled water, to give a precipitate on the addition of lime water. It ought not, after being acidulated with pure nitric acid, to give a precipitate with nitrate of baryta nor with nitrate of silver. Sulphuretted hydrogen ought not to impart to it the slightest colour, and on the addition to it of a few drops of a solution of ammonio-sulphate of copper, a black precipitate ought not to be formed.

14. *Chloride of ammonium.*—This salt ought to volatilize completely when ignited on platinum foil; its solution ought to be neutral to test paper, and it ought to give no precipitate nor coloration on the addition of sulphide of ammonium.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

15. *Sulphide of ammonium* (hydrosulphuret of ammonia) is prepared by passing hydrosulphuric acid through liquid ammonia until it does not produce a precipitate in a solution of

sulphate of magnesia. It ought not to produce a precipitate with a solution of lime, and it ought to leave no residue on evaporation to dryness and ignition.

Dilute one part with three of water.

16. *Carbonate of ammonia* must competely volatilize. Its solution ought to give no precipitate or coloration with sulphide of ammonium, nor with sulphuretted hydrogen after acidulation with hydrochloric acid. Its solutions after being acidulated with nitric acid ought to produce no precipitate with nitrate of baryta nor with nitrate of silver.

Dissolve one part, by weight, of the salt, in four parts, by measure, of water, and add one measure of ammonia.

17. *Arseniate of ammonia* is prepared by neutralizing arsenic acid with carbonate of ammonia, and evaporating to dryness.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

Arsenic acid is prepared by dissolving arsenious acid in nitric acid, mixed with a little hydrochloric acid, evaporating the solution to dryness, and igniting somewhat below a *low* red heat, until all nitric acid is expelled.

18. *Molybdate of ammonia.*—Digest molybdic acid in ammonia until complete solution is effected; filter the colourless fluid. Solution of molybdate of ammonia, mixed with nitric acid or hydrochloric acid until the precipitate which forms at first is redissolved, must remain colourless upon boiling. If it acquires a yellow tint, the reagent contains phosphoric acid, and is unfit for use (supposing always, of course, that the hydrochloric or nitric acid was perfectly pure).

19. *Sulphate of potash.*—Recrystallize the sulphate of potash of commerce, dissolve one part, by weight, of the purified salt, in two hundred parts, by measure, of water.

20. *Nitrite of potash* is prepared by fusing one part of nitrate of potash in an iron pan, then adding two parts of lead, and keep stirring the mixture with an iron rod. The lead oxidizes in a great measure, even at a dull-red heat, changing to a yellow powder. To oxidize the last remaining particles of the metal, increase the heat to visible redness. The mixture

generally takes fire; there is, however, no danger, at least when no more than a quarter of a pound of nitrate of potash has been used. Let the mass cool, and then treat it with cold water to dissolve out the soluble part; filter this solution, and conduct carbonic acid into the filtrate. This serves to precipitate nearly the whole of the oxide of lead that has passed into the solution; a little sulphide of hydrogen will remove the remainder. Filter again, and evaporate the filtrate to dryness, stirring the mass towards the end of the operation; heat the dry residue to fusion, to destroy any hyposulphite of potash that may have been formed. It must, upon addition of dilute sulphuric acid, copiously evolve nitric oxide gas.

Dissolve one part of the fused mass in two parts of water.

21. *Ferrocyanide of potassium* (yellow prussiate of potash). —Dissolve one part, by weight, in twelve, by measure, of water.

22. *Ferricyanide of potassium* (red prussiate of potash).—Dissolve one part, by weight, of the salt, in twelve parts, by measure, of water.

23. *Sulphocyanide of potassium.*—Dissolve one part of the salt in ten parts of water.

24. *Chromate of potash* in solution ought not, after it has been acidulated with hydrochloric acid, to give a precipitate with chloride of barium.

Dissolve one part, by weight, in eight parts, by measure, of water.

25. *Caustic soda* is prepared by dissolving one part, by weight, of carbonate of soda, in twelve parts, by measure, of water, and boiling the solution in a clean iron pan. Hydrate of lime must be added in small portions to the boiling liquid, until hydrochloric acid causes no effervescence in a portion of the liquid. When this point has been attained, the pan must be removed from the fire, and the precipitate allowed to subside. The supernatant liquid must then be drawn off by means of a syphon, or passed through a filter of bleached linen, and the filtrate evaporated rapidly over a quick fire until it has been reduced to half its original bulk. On supersaturating

a portion of the liquid with hydrochloric acid, no, or only a slight, effervescence should take place. Sulphide of hydrogen must not produce a precipitate or coloration in its solution. The solution must be kept in well-stoppered bottles.

26. *Carbonate of soda* in solution ought not, after it has been acidulated with nitric acid, to give a precipitate with chloride of barium nor with nitrate of silver.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

27. *Phosphate of soda* must form no precipitate with ammonia.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

28. *Acetate of soda* is made by adding acetic acid to a concentrated solution of carbonate of soda until all effervescence ceases. This solution must be free from sulphuric acid.

Dilute one part of the concentrated solution with four parts of water.

29. *Chloride of barium.*—A solution of this salt must be neutral to test paper; after precipitation by sulphuric acid, the filtrate ought not to leave the slightest residue when evaporated on platinum foil. Its solution ought not to give a precipitate or be coloured by the addition of sulphide of hydrogen or by sulphide of ammonium.

Dissolve one part of the salt in ten of water.

30. *Nitrate of baryta.*—A solution of this salt must not be rendered turbid by nitrate of silver; for other impurities, test as directed in the chloride.

Dissolve one part of the salt in ten parts of water.

31. *Lime water* is made by digesting recently prepared hydrate of lime for some time with cold distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, decant subsequently, and keep the clear fluid in well-stoppered bottles.

32. *Chloride of calcium* is made by dissolving pure carbonate of lime in dilute hydrochloric acid; the solution thus obtained must be neutral to test-paper; and it must not form a precipitate, nor be coloured by sulphide of ammonium.

Dilute one part of the concentrated solution with five parts of water.

33. *Sulphate of lime* (gypsum).—Dissolve as much of the salt as the water will take up.

34. *Sulphate of magnesia* (Epsom salts).—Dissolve one part in eight of water.

35. *Perchloride* (sesquichloride) of iron is prepared by dissolving recently precipitated and well-washed peroxide of iron in hydrochloric acid. It must not contain any free acid.

36. *Acetate of lead.*—Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

37. *Subnitrate of mercury* is made by heating gently in a small flask nine parts of nitric acid in conjunction with ten parts of mercury, until the disengagement of nitrous fumes ceases; the solution is then boiled for some time with the undissolved portion of the mercury, care being taken to replace the water lost by evaporation. The crystals, which separate on the cooling of the liquid, are dissolved in twenty parts of cold water, slightly acidulated with nitric acid. The fluid is then filtered, if necessary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

38. *Chloride of mercury.*—Dissolve one part of the salt in sixteen parts of water.

39. *Sulphate of copper.*—Dissolve one part of the pure crystallized sulphate in ten parts of water.

40. *Nitrate of silver.*—Dissolve one part, by weight, of the salt, in twenty parts, by measure, of water.

41. *Nitrate of cobalt.*—Dissolve one part in ten parts of water.

42. *Solution of indigo.*—"Take from 4 to 6 parts of fuming sulphuric acid, add slowly and in small portions at a time, 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo blue is thereby destroyed; it is therefore advisable when dissolving larger quantities of the substance to place the

vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into twenty times the quantity of water, mix, filter, and keep the filtrate for use."

43. *Distilled water* ought always to be employed in all the above solutions and in all analytical operations. It should leave no residue on evaporation, and should give no precipitate, or even turbidity, with chloride of barium, nitrate of silver, oxalate of ammonia, or lime water.

44. *Reagent papers.* Blue litmus paper serves to detect the presence of free acids or of acid salts in fluids, since they change the blue colour to red. Reddened litmus paper serves to detect the presence of free alkalies,* and of earths and salts possessing an alkaline reaction, by changing the red colour to blue. Turmeric paper aids, like reddened litmus paper, in the detection of free alkalies, &c., by changing its yellow colour to brown.

Preparation of blue litmus paper. "Digest one part of litmus of commerce with six parts of water, and filter the solution; divide the intensely blue filtrate into two equal parts; saturate the free alkali in the one part, by repeatedly stirring with a glass rod dipped in very dilute sulphuric acid, until the colour of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of fine, unsized paper through it; suspend these strips over threads, and leave them to dry. The colour of litmus paper must be perfectly uniform, and neither too light nor too dark."

Preparation of reddened litmus paper. "Stir blue solution of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid has just turned distinctly red. Steep slips of paper in the solution, and dry them as directed in the preceding paragraph. The dried slips must look distinctly red."

Preparation of turmeric paper. "Digest and heat one part of bruised turmeric root with six parts of weak spirit of wine, filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

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* Dr. Taylor states that a very delicate test-paper for detecting alkalies may be prepared by steeping slips of paper in an acid infusion of rose petals.

94. LIST OF THE REAGENTS EMPLOYED IN THE DRY STATE.

45. *Nitrate of ammonia* is made by neutralizing nitric acid with carbonate of ammonia. The solution is evaporated until crystals begin to be deposited, and is then allowed to cool. The crystals are collected and placed in well-stoppered bottles.

46. *Cyanide of potassium* must be of a milk-white colour, and perfectly free from any admixture of iron.

47. *Sulphate of iron* is principally employed for the detection of nitric acid.

48. *Copper turnings* are likewise employed for the detection of nitric acid.

49. *Carbonate of soda* must not contain any sulphuric or hydrochloric acid.

50. *Biborate of soda* (borax) is employed in blowpipe analysis. It should be heated below the fusing point to drive off its water of crystallization, and then powdered.

51. *Phosphate of soda and ammonia* (microcosmic salt) is likewise employed as a reagent in blowpipe analysis.

APPARATUS.

95. The processes employed in qualitative analysis are exceedingly simple, and do not require much apparatus for their execution. The small amount actually requisite is described in the following list, and may be procured in the shops of operative chemists.

1½ dozen test tubes.
Test-tube stand.
2 small evaporating dishes.
Washing bottle.
Spirit lamp.
2 watch-glasses.
Rat-tail and triangular file.
Platinum wire and foil.
Sulphuretted hydrogen apparatus.
Small retort stand.
3 small glass funnels.
2 porcelain crucibles.
½ lb. glass tubing.
¼ lb. glass rod.
Small mortar and pestle.
1 quire filtering paper.
Crucible tongs.
Black's blowpipe.
Tube cleaner.

A number of best corks.
A few lengths of small vulcanized tubing.
Small german beakers.
Litmus paper, blue and red.
Turmeric paper.

96. Having explained the different operations employed in analysis, we will resume our previous subject. It has been stated already, that if, to a solution of any of the soluble salts of the insoluble bases, a soluble base is added, the soluble base will take away the acid from the insoluble base; the latter (viz., the insoluble base) being set free, will consequently precipitate, on account of its insolubility in the liquid. If, then, we were to add the exact quantity of the soluble base required for the complete decomposition of the salt, and no more, all the soluble base we added would be combined with the acid of the original salt, and all the acid of the original salt would be combined with the soluble base—in other words, neither the acid of the salt nor the soluble base would either of them be in excess, but the entire amount of the one would be in combination with the entire amount of the other. It is impossible in practice to add the reagents with such mathematical accuracy; we are therefore obliged to add, in order to ensure the complete decomposition of a salt of this kind, the soluble base in excess; and *in this excess*, or in this *uncombined portion*, some of the insoluble bases dissolve, being soluble in the free soluble bases. One of the insoluble bases (oxide of zinc) is soluble both in the volatile and fixed alkalies; some of the others are soluble in ammonia, but insoluble in the other two; some are soluble in potash and soda, but insoluble in ammonia; others are insoluble in each of the three alkalies. And there are some which, although insoluble in ammonia, are not precipitated by it, if salts of ammonia are present, and are only partly precipitated by the fixed alkalies under these circumstances.

97. The properties which the insoluble bases display, with regard to ammonia and the fixed alkalies, are exhibited in the table (page 41), which the student must study with the aid of the experiments.

TABLE SHOWING THE SOLUBILITY OF THE BASIC OXIDES AND THEIR HYDRATES.

Names.	Symbols.	Names.	Symbols.
Soluble in water.			
Hydrate of potash } *white*	KO, HO	Hydrate of baryta } *white*	BaO, HO
Hydrate of soda	NaO, HO	Hydrate of strontia	SrO, HO
		Hydrate of lime	CaO, HO
The rest are insoluble in water.			
Soluble in ammonia and the fixed alkalies.			
Hydrate of zinc (*white*)			ZnO, HO
Insoluble in ammonia and the fixed alkalies.			
Hydrate of the sesquioxide of iron (*reddish brown*)	Fe_2O_3, 3HO	Suboxide of mercury (*forms no hydrate*)	Hg_2O
Hydrate of bismuth (*white*)	BiO_3, 3HO	Hydrate of the protoxide of mercury (*yellow*)	HgO, HO
Insoluble in ammonia, soluble in the fixed alkalies.			
Hydrate of alumina } *white*	Al_2O_3, 3HO	Hydrate of the sesquioxide of chromium (*bluish green*). (This oxide is insoluble in boiling solutions of the fixed alkalies.)	Cr_2O_3, 3HO
Hydrate of the protoxide of tin	SnO, HO	Hydrate of lead (*white*). (This hydrate is only very slightly soluble in the fixed alkalies.)	PbO, HO
Hydrate of the peroxide of tin	SnO_2, HO		
Oxide of antimony	SbO_3		
Soluble in ammonia, insoluble in the fixed alkalies. The presence of ammoniacal salts prevents some of them from being completely precipitated by the fixed alkalies.			
Hydrate of cobalt (*pale red*)	CoO, HO	Hydrate of copper (*whitish green*). (If the fixed alkalies are added to cold solutions of copper salts, the hydrate is precipitated; if added to boiling solutions, the anhydrous oxide is precipitated)	CuO, HO
Hydrate of nickel (*green*)	NiO, HO		
Oxide of silver (*forms no hydrate*)	AgO		
Hydrate of cadmium (*white*)	CdO, HO		
Insoluble in ammonia and the fixed alkalies; but in the presence of salts of ammonia the volatile alkali cannot precipitate them, and the fixed alkalies only do so in part.			
Hydrate of magnesia (*white*)	MgO, HO	Hydrate of protoxide of iron is of a white colour, which, on exposure to the air, finally becomes red, owing to its being converted into the peroxide.	FeO, HO
Hydrate of manganese (*white*), speedily becoming brown by absorbing oxygen from the air, and becoming converted into a higher oxide	MnO, HO		

Ammonia does not precipitate the hydrate from solutions of protoxide of mercury, but a white precipitate having the following composition ($Hg\ NH_2 + HgO$); the fixed alkalies likewise throw down the same precipitate, if salts of ammonia are present, but in the absence of these salts, they precipitate the hydrate.

98. To a solution of sesquichloride of iron add a solution of caustic soda in excess; hydrate of the sesquioxide of iron will precipitate, and will not be redissolved by an excess of the caustic soda.

99. To a solution of sesquichloride of chromium add a *cold* solution of caustic soda, until the precipitate which first appears is redissolved; then boil the solution until the hydrate of the sesquioxide of chromium once more precipitates.

100. Add to a solution of sulphate of alumina caustic soda, until the precipitate which first forms is redissolved; then add hydrochloric acid until the solution manifests an acid reaction; and, finally, ammonia in excess, which will cause the precipitation of hydrate of alumina.

101. We will now attempt to show how the precipitation or the volatilization of one substance and the non-precipitation or non-volatilization of another, under the same circumstances, is applied in analysis in the separation and detection of substances. Limiting our observations to the bases, we must first inquire in what state they can be precipitated.

102. The *soluble bases* can only be precipitated from their solutions in the form of salts; therefore, if we wish to precipitate a soluble base from its solution, whether it exists in the solution uncombined or as a salt, we must add to the solution *some acid*, or some salt containing *an acid*, which acid will form, with the soluble base, a salt *insoluble* in the solution from which it has to be precipitated, whether the solution be acid, alkaline, or neutral. Now, if a salt, insoluble in *the state the solution is in*, cannot be formed, we must alter the properties of the solution to effect the precipitation; for instance, if the solution is acid, and the salt of the base we wish to precipitate is soluble in acids, we must first neutralize the solution by some base, before attempting the precipitation.

103. The *insoluble bases* must, if in solution, be in the form of salts; those of them, however, which are soluble in the volatile or fixed alkalies, can also be present in solution, by being dissolved in the alkalies in which they are soluble. The insoluble bases can be precipitated from the solution of their

soluble salts, either as *insoluble salts* or in an *uncombined state;* therefore, to precipitate the insoluble bases from the solutions of their soluble salts, we must add *some acid*, or a *salt containing an acid*, which will form with them a salt perfectly *insoluble* in the solution; or we must add *some soluble base* in an excess of which the insoluble base does not dissolve. We can precipitate them from their *alkaline solutions* by adding a *free acid*, which forms with them an insoluble salt; but, in the generality of cases, they cannot be precipitated from their alkaline solutions by a *salt*, the acid of which forms with them a salt insoluble in a neutral or acid solution, or by a *soluble base* in which they are insoluble; before they can be precipitated from alkaline solutions either by *salts* or *bases*, we must, in the generality of cases, *neutralize* the alkali, in which they are dissolved, by some acid. (Experiment, paragraph 100.)

104. The *volatile base*, ammonia, if in the free state, is at once distinguished by the smell; but when it is present in solution, in the form of a salt, the salt must be decomposed by the addition of some stronger base, before the ammonia can be detected.

105. We will now give a few examples* as illustrations. Suppose we had to examine a liquid for baryta and lime: they might be present in the solution either in the uncombined state or as salts; and as chromate of baryta is insoluble, and chromate of lime soluble, we might add to the solution a soluble chromate—say, chromate of potash. If we obtained a precipitate by the soluble chromate, baryta must be present; if we obtained no precipitate, it must be absent: to the filtrate from the chromate of baryta precipitate, or to the solution which has failed to give a precipitate with the soluble chromate, we must add some acid, or a salt containing an acid, which forms with lime an insoluble salt—say we add oxalic acid or oxalate of ammonia; if either of these reagents produces a

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* The teacher ought to give the student three or four solutions on each example; some of the solutions containing one of the substances named in the example, some containing both of the substances named in the example.

precipitate, lime is present; if it does not produce a precipitate, lime is absent. Suppose we had to examine a solution for sesquioxide of iron and alumina: now, if the sesquioxide of iron was present in the solution, the liquid could not have an alkaline reaction,* because sesquioxide of iron is insoluble both in the volatile and fixed alkalies; therefore, if the solution is alkaline, from one of the fixed alkalies, sesquioxide of iron must be absent; if the alkalinity be due to the volatile alkali, alumina, as well as sesquioxide of iron, must be absent, because alumina, as well as sesquioxide of iron, is insoluble in ammonia. We will suppose that the solution is slightly acid, then both substances may be present; we add to the solution one of the fixed alkalies in excess, the excess will keep the alumina in solution, but the sesquioxide of iron will be precipitated. The solution must be filtered, if a precipitate is formed; and to the filtrate, or to the solution which has failed to give a precipitate, must be added hydrochloric acid in excess: if ammonia is then added in excess, alumina, if present, will be precipitated. Suppose we had to examine a solution for ammonia and potash: as the same reagents which precipitate potash precipitate also ammonia, the latter, when present, must be got rid of before potash can be tested for; we are therefore obliged to look for ammonia first; to ascertain if it is present, we add to a part of the solution some soluble base, as potash or soda; if present, it will be liberated from its combinations by either of these reagents, and can then be detected by the smell, &c. When present, the other portion of the solution must be evaporated to dryness, and the ignition continued until all the ammoniacal salt is expelled; if, after the expulsion of the ammoniacal salt, a residue remain, it must be dissolved in water, and examined for potash by tartaric acid or bichloride of platinum.

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* Unless fixed organic matter was present, which is a condition it would be improper to consider or notice at present.

HOW THE WORK IS TO BE STUDIED.

106. The mode of separating one substance from another, and the properties and appearances of the precipitates, are the first things to be studied in qualitative analysis. The student gains this preparatory knowledge by performing the different experiments pointed out in the *special tables*, carefully noting the reactions which the reagents give with each individual member, and explaining by diagrams the decompositions produced.

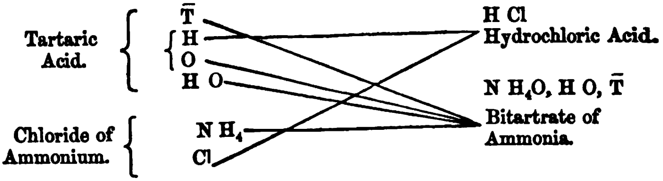
107. These remarks may be illustrated by an example. The first group, and therefore the one which first claims the attention of the student, is made up of three members, viz., POTASH, SODA, and AMMONIA. In *the first paragraph*, under the head AMMONIA, it is stated that this substance and its salts are *volatile*, *i.e.* they can be converted by heat into vapour. In the second paragraph it is stated that all salts of ammonia are decomposed on the addition of a stronger base, gaseous ammonia being given off. In the third, that *tartaric acid* produces, in neutral and alkaline solutions of ammonia, a white, crystalline precipitate of bitartrate of ammonia. He has, therefore, to perform and verify these experiments, to notice those conditions which favour the reactions and those which prevent their development.

108. Let *bitartrate of ammonia* be taken as an example of what has just been said. It is stated in the table that this precipitate is produced both in neutral and alkaline solutions, but that free alkalies and free mineral acids dissolve it. Hence it follows, that though tartaric acid produces a precipitate in alkaline solutions, it can do so only when it is added in excess; because, as free alkalies dissolve the precipitate, they must, when present, prevent its formation. It is also evident that tartaric acid cannot detect ammonia in the presence of free mineral acids, for the same reason.

109. The conditions which favour or prevent precipitation,

together with the appearances of the precipitates, must therefore be carefully remembered by the student. This is best accomplished by recording them in a note-book at the time the experiments are made, together with diagrams of the decompositions which the different substances undergo on the addition of the reagents.

110. To exemplify what we wish to convey respecting decompositions, we select chloride of ammonium, and show by a diagram the change which this salt undergoes when tartaric acid is added to it, thus—



111. The student having performed all the experiments under ammonia, potash, and soda, must found upon them a method for detecting these three substances when they occur together, and then compare it with the one given in the text. By adopting this plan, a more extensive and accurate knowledge will be acquired than if the method given in the work be immediately consulted. Several solutions are then given to him, each of which he must examine for the members of this group. When he can perform these practical exercises correctly, he may pass on to the second group, performing the experiments given in that table in the same manner. He must deduce from them the method for separating the members of this group from each other, and again test his acquired knowledge by practical exercises. When he thoroughly comprehends the way of separating them from one another, he will find, by the aid of the *general table* (Chapter III), the method to be employed for separating this group from the first. He should then examine various solutions, which may contain all the members of the first two groups. When he has completed all the basic groups in the manner described, he

should analyse about twenty different solutions, and look for all the bases given; after which, the experiments given under the different acids must be performed. The student is then in a condition to go through a complete course of *qualitative analysis*, commencing with substances already in a state of solution, and concluding with the examination of solids. Both in the solutions and solids he must look for all the acids and bases treated of in the work.

112. SOURCES OF ERROR.—One frequent source of error with the young analyst has already been noticed, viz., the imperfect mixture of the reagents with the solutions to which they are added. Another prolific source of error is the too liberal or the too sparing addition of the reagent, both being objectionable. To show the objectionable nature of a too sparing addition of the reagent, we will suppose the student to be examining a solution for baryta and lime; we will further suppose he has added chromate of potash and obtained a precipitate,* which proves the presence of baryta. He filters, and to the filtrate he adds oxalate of ammonia, to test for lime; he obtains a precipitate with oxalate of ammonia, although lime is absent, because he has not added sufficient quantity of the chromate of potash to precipitate all the baryta: thus, by the imperfect addition of a reagent, he arrives at a wrong conclusion. This fruitful source of error, viz., imperfect precipitation, may be avoided by adding to the filtrate a little more of the reagent with which the precipitation was effected. If this produces no further precipitate, the substance has been fully precipitated. Should a further precipitate be produced, it must be removed by filtration before attempting to throw down any other substance. The student must also carefully distinguish between the terms *precipitate* and *filtrate*, and be very particular in thoroughly washing the precipitates which

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* Whenever a precipitate is obtained, it must be separated from the fluid by *filtration*, if either the fluid or the precipitate has to be examined further; the fluid for other substances, the precipitate for the detection of the several substances which may have been precipitated, or for the confirmation of any one substance.

require further examination. The wash-water must not be collected with the filtrate, if this last should be required for further examination. But all these precautions will have been attended to in vain should the experiments be performed in dirty apparatus, this being sufficient of itself to nullify all satisfactory results.

113. SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.—A qualitative investigation may be made with a two-fold view, viz.—either, 1st, to prove that a certain definite body is or is not contained in a substance (*e.g.* lime in a mineral water); or, 2d, to ascertain all the constituents of a chemical compound or a mixture. A few simple experiments enable us to determine the first; but if we wish to discover all the constituents of a chemical compound or a mixture, if we intend to prove that, besides certain bodies which we have detected, no other substance can be present, we must know *not only the behaviour of the different substances we are to look for with the reagents* we shall employ, but we must know also the order and succession in which the reagents are to be applied.

114. It would be very difficult, if not impossible, to examine a solution for all the bases, if we were obliged to precipitate them singly from the solution, because it would be impossible to meet with, for each base, a reagent that would only precipitate that base and no other. For this and other reasons we divide the bases into families or groups; the acids are also divided into groups, but their division is more imperfect than that of the bases. The separation into groups is effected by observing some property common to several substances and peculiar to them, by which means a group is formed possessing distinctive characteristics which distinguish its members from the *lower* groups. Most important advantages are gained by a distribution of this kind, as it would be impossible to analyse complex substances accurately without some such division; for as many of the reagents precipitate more than one substance, it would be difficult to decide in such cases what the particular substances were which had been precipitated, and whether they had all been detected.

Another important advantage arising from this arrangement is, that it is as easy to discover a group as an individual substance; and the absence of a group being proved, it is unnecessary to examine further for any member contained in it.

115. We have divided the bases into the following six groups:—

GROUP VI.

1st Division.

Oxide of Silver.
Suboxide of Mercury.
Oxide of Lead.

2d Division.

Oxide of Lead.
Protoxide of Mercury.
Oxide of Bismuth.
Oxide of Cadmium.
Oxide of Copper.

GROUP V.

Arsenious Acid.
Arsenic Acid.
Oxide of Antimony.
Protoxide of Tin.
Peroxide of Tin.
Peroxide of Gold.
Peroxide of Platinum.

GROUP IV.

Alumina.
Sesquioxide of Chromium.
Protoxide of Iron.
Sesquioxide of Iron.

GROUP III.

Oxide of Zinc.
Oxide of Manganese.
Oxide of Nickel.
Oxide of Cobalt.

GROUP II.

1st Division.

Baryta.
Strontia.
Lime.

2d Division.

Magnesia.

GROUP I.

Potash.
Soda.
Ammonia.

116. When the different substances have been divided into groups, each group is divided and subdivided, until the individual detection of the various substances present is finally accomplished.

117. ARRANGEMENT OF THE RESULTS OF THE ANALYSIS.—The student, during the course of his analytical studies, ought invariably to record the results of each analysis in his note-book, in a systematic and tabular form. An illustration is given to show the method to be pursued.

118. PRELIMINARY EXAMINATION OF A SOLID SUBSTANCE.—1st. It is a colourless, crystallized substance, probably a salt. 2d. Heated alone on charcoal, it deflagrates; a white, infusible substance remaining behind, which becomes luminous, and imparts a crimson colour to the flame, probably strontia. 3d. Soluble in water; the solution is neutral to test-paper. As it is soluble in water, a large number of substances, all the insoluble salts, must be absent; as it is neutral to test-paper, all the salts of the alkalies and alkaline earth having an alkaline reaction must be absent; and the soluble salts of the other metals, with the exception of manganese and silver, must be absent, because their soluble neutral salts redden blue litmus paper.

119. The preliminary experiments indicate the presence of nitrate of strontia.

EXAMINATION FOR ACIDS.

120. The following acids, viz., CO_2, HS, AsO_3, AsO_5, and CrO_3, were proved to be absent on the examination for the bases.

121. The remainder of the acids, which give precipitates with a salt of baryta, could not be present; as they likewise form, with strontia, insoluble salts.

122. Added to a portion of the original solution AgO, NO_5, no precipitate; absent, Cl, Cy, Br, and I.

123. Added to another portion HO, SO_3, and copper turnings, nitrous fumes were evolved, showing the presence of nitric acid.

124. The examination for chloric acid yielded a negative result.

ACTUAL EXAMINATION.

On the addition of hydrochloric acid, no effervescence; absence of CO_2 and HS.

<table>
<tr>
<td rowspan="4">H Cl.
No precipitate.
Absent:
Ag O,
Hg_2 O,
and probably
Pb O.</td>
<td rowspan="4">H S.
No precipitate.
Absent:
Hg O,
Pb O,
Bi O_3,
Cd O,
Cu O,
and
As O_3
As O_5
Sn O
Sn O_2
Sb O_3
Pt O_2
Au O_3</td>
<td rowspan="4">Boiled to expel H S; added a few drops of HO, NO_5; again boiled; added, lastly, NH_4 Cl, and NH_4 O. No precipitate.
Absent:
Fe_2O_3, Al_2O_3, and Cr_2O_3
The substance being soluble in water, the phosphates and oxalates of the alkaline earths could not be present.</td>
<td rowspan="4">NH_4 S.
No precipitate.
Absent:
Mn O
Zn O
Ni O
Co O.</td>
<td colspan="2">NH_4 O, CO_2.
A white precipitate formed.</td>
<td colspan="2">Divided the filtrate into two portions.</td>
</tr>
<tr>
<td colspan="2">May be present:
BaO, CO_2, Sr O, CO_2, CaO, CO_2; dissolved in HO, $\bar{A}$; divided into two portions.</td>
<td>To one portion added. $3NH_4$ O, As O_5.</td>
<td>Evaporated the other portion to dryness, to expel ammoniacal salts. No residue.
Absent:
NaO, KO.</td>
</tr>
<tr>
<td>To one portion added CaO,SO_3</td>
<td>Precipitated the Sr O from the other portion by HO, SO_3.</td>
<td rowspan="2">No precipitate.
Absent:
Mg O.</td>
<td>Boiled a portion of the original solution with NaO, HO.</td>
</tr>
<tr>
<td>A precipitate, after lapse of sometime presence of Sr O, absence of Ba O.</td>
<td>Added to the filtered liquid NH_4 O, and HO, $\bar{O}$.
No precipitate. Absent: Ca O.</td>
<td>No ammonia evolved; absence of ammoniacal salts.</td>
</tr>
</table>

CHAPTER II.

SPECIAL PROPERTIES OF THE BASIC GROUPS.

FIRST GROUP.

POTASH. SODA. AMMONIA. (LITHIA.)

125. The members of this group are called alkalies. They are readily soluble in water in their pure (caustic) state. The solution restores the blue colour of reddened litmus paper, and imparts an intensely brown colour to turmeric paper; the solution of their sulphides and carbonates acts in a similar manner upon vegetable colours.

126. Potash and soda are oxides of the metals *potassium* and *sodium;* these metals are lighter than water, and decompose it at the ordinary temperature. Ammonia (NH_3), being a gas of a very pungent odour, is readily distinguished from all the other bases: it dissolves freely in water, and may be again expelled on boiling the solution. Ammonia, when dissolved in an aqueous solution, unites with one atom of water, forming NH_4O, the oxide of an hypothetical compound metal, *ammonium* (NH_4).

127. Potash cannot be detected by means of reagents in the presence of ammonia or any of its salts; because the same reagents which precipitate potash from its solutions form also, with ammonia, a corresponding class of insoluble substances (A 3 and B 3); the latter must therefore be *expelled* from the substance under examination, before proceeding to test for the former. The method for expelling the ammonia is described in paragraph 138.

128. HOW TO ASCERTAIN THE PRESENCE OR ABSENCE OF EACH OF THE THREE MEMBERS OF THIS GROUP IN A SOLUTION WHICH CAN ONLY CONTAIN THESE THREE BASES.—As the presence of ammonia interferes, as before stated, with the detection of potash, we are always obliged, on this account, to look for ammonia before we look for potash. And as the reagent for the detection of ammonia would interfere (A 2) with the detection of the two other members of the group, we are obliged, on this account, to look for the ammonia in a *portion* only of the solution under examination. For these reasons, then, we divide the solution into two parts, which we shall call A and B.

129. In A we *examine* for AMMONIA, according to the method described in A 2 and paragraph 136. The method there described is the characteristic test for ammonia; in that way it can be distinguished from all other substances. As the absence or presence of ammonia regulates our mode of search for the two other members of the group, we must describe the mode of proceeding to be adopted when it is *absent*, as well as when it is *present*.

130. *If it is absent*, the B portion of the solution is examined for SODA and POTASH in the following way,—a *clean* (*see* Precautions, paragraph 133) platinum wire is dipped into the solution, and then introduced into the melting zone of the flame of a Bunsen's gas lamp (see paragraph 67), or the inner flame of a spirit lamp. If the flame is coloured *yellow*, SODA is present; if it is coloured *violet*, it proves the absence of SODA (C 4) and the probable presence of POTASH (B 4). *If soda is present*, examine for potash by the photo-chemical method (paragraph 142). The *presence of potash* may be *confirmed* by adding to the solution under examination, which must be cold (B 3), a solution of *tartaric acid* or *bitartrate of soda* (*see* paragraph 140) in excess, and shaking the mixed liquid very violently, and then allowing it to rest for some time; if a crystalline precipitate appears after this, POTASH is present (B 3). The time required for the appearance of the crystalline precipitate depends upon the quantity of potash in the solu-

tion; if the quantity of potash is small, the precipitate may not appear until several hours after the addition of the reagent.

131. *If ammonia is present*, the B portion of the solution must be evaporated to dryness and *ignited*, in order to volatilize the ammonia or its salts (A 1, and paragraph 138); the ignition must be continued as long as any white fumes or smoke are evolved. If a residue remains, after the ammonia or its salts are expelled, one or both of the other two members of the group are present; this residue must be dissolved in the smallest possible quantity of water, and *examined* for POTASH and SODA, in the way described in the preceding paragraph.

132. WHEN THE EXAMINATION IS NOT CONFINED TO THE ALKALIES, BUT ALL, OR, AT LEAST, SOME OF THE OTHER BASES HAVE TO BE SOUGHT FOR IN THE SOLUTION, the solution, after being freed from all the other bases but those of the first group must be evaporated to dryness, and ignited, to expel the ammoniacal salts, which have been added for their discovery. If a residue remain,* after the vapour of the ammoniacal salts has ceased to be evolved, it must be examined for potash and soda, in the way described in paragraph 130. In this case—that is, when other bases besides those of the first group have to be sought for—AMMONIA is to be tested for in a part of the *original solution*.

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* A fixed residue is not a certain proof of the presence of potash or soda, as it may arise from the presence of one of the non-volatile acids, viz., phosphoric, boracic, or silicic acid. (*See* paragraph 19.)

TABLE I.

BEHAVIOUR OF THE FIRST GROUP WITH THE SPECIAL REAGENTS.

AMMONIA $(N H_4 O)$.	POTASH $(K O.)$	SODA $(Na O)$.
A 1. Ammonia and its salts are *volatile*. (*See* par. 138.)	B 1. Potash and its salts are *not volatile*.	C 1. Soda and its salts are *not volatile*.
A 2. All salts of ammonia are *decomposed* with the liberation of free ammonia, when any stronger base, such as *lime*,* *potash* or *soda*, is added to their solutions. If the liquid be gently heated, the ammonia is volatilized, and its presence may then be recognised in three distinct ways. *a*. By its pungent *odour*. *β*. By turning *red* litmus paper *blue*. *γ*. By forming *white fumes*, when any volatile acid, as hydrochloric acid is brought into contact with it.†	B 2. When salts of potash are decomposed by a stronger base, the potash which is liberated, *not being volatile* like ammonia, cannot be detected in a similar way.	C 2. When soda salts are decomposed by a stronger base, the soda which is liberated, *not being volatile* like ammonia, cannot be detected in a similar manner.
A 3. *Tartaric acid* $(2 H O, C_8H_4O_{10}=2 H O, \overline{T})$, in solution, produces in neutral or alkaline solutions of ammonia a white crystalline precipitate of BITARTRATE OF AMMONIA $(N H_4 O, H O, \overline{T})$, which is rather more soluble in water than the corresponding potash salt. Vigorous shaking promotes the formation of this and the corresponding potash salt.	B 3. *Tartaric acid*, in solution, throws down from neutral or alkaline solutions of potash a white crystalline precipitate of BITARTRATE OF POTASH $(KO, HO, \overline{T})$. This salt, and the corresponding one of ammonia, are soluble in free alkalies and free mineral acids. Slightly soluble in cold, much more so in hot water. (*Consult* par. 140.)	C 3. *Tartaric acid*, in solution, produces no precipitate in solutions of soda, except in *extremely* concentrated solutions, bitartrate of soda being soluble.
A 4. Ammonia and its salts impart to a lamp flame *no* characteristic colour.	B 4. Potash and its salts tinge the outer lamp flame VIOLET. (*Consult* par. 142.)	C 4. Soda and its salts impart to the outer lamp flame an intense YELLOW colour. Small quantities of soda can by this means be detected in the presence of much potash, the yellow flame overpowering the violet. (*See* par. 147.)

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* If lime is employed, it must be the solid hydrate, not a solution of lime (lime water).

† This experiment is best performed by inserting a glass rod moistened with hydrochloric acid into the mouth of the test-tube in which the decomposition of the ammonia salt has been effected. The hydrochloric acid employed should not be concentrated, but should be diluted with an equal volume of water. *Consult* paragraph 136.

133.—*The following precautions are to be attended to in the analysis of this group.* In testing for ammonia, one error frequently committed is, that of allowing the glass rod to remain so long in the heated atmosphere of the test-tube, that on its removal a *sensible evaporation* takes place from its surface, which is mistaken for the white fumes which are formed when any volatile acid is brought in contact with ammonia. To avoid this error, the solution which is under examination should be heated until it approaches the boiling point, but should not actually be boiled, and the moistened glass rod should, immediately after its insertion into the test-tube, be withdrawn. If any fuming should then arise, it can only proceed from the presence of ammonia, which must be confirmed by the other appropriate tests. Young students seldom continue the ignition for the expulsion of the ammoniacal salts sufficiently long; consequently they find potash when it is not present, owing to the unexpelled ammonia giving precipitates with tartaric acid and bichloride of platinum. The attention of the student is therefore directed to paragraph 138. The detection of potash by tartaric acid requires, in the first place, that the solution be neutral or alkaline, not acid, and as concentrated as possible. The reagent must then be added in excess (if the fluid is alkaline the tartaric acid must be added until the solution is acid), and the fluid well agitated. The application of heat must be avoided, and time allowed for the appearance of the precipitate, as it becomes visible only after the lapse of some hours, when small quantities of potash are present. In testing for potash or soda by the lamp flame, it is necessary that the platinum wire should be perfectly clean. This can only be secured by directing the blowpipe flame upon it until it ceases to impart a colour; care should then be taken not to touch, even with the fingers, that end of it on which the substance is to be placed.

SPECIAL REMARKS.

134. Ammonia.—This substance is a gas, transparent and colourless, of a very pungent and peculiar smell and taste.

It is instantly absorbed by water, forming the solution of the gas called *aqua ammoniæ*. If this liquid is boiled, the gas is expelled. When organic substances containing nitrogen decay and putrefy, carbonate of ammonia is constantly produced. The same salt is likewise formed when nitrogenized organic substances are submitted to destructive distillation.

135. When any volatile acid is brought into an atmosphere of ammonia, they unite together, forming a solid salt; this is the white fumes observed in testing for ammonia.

136. Ammonia may be liberated from its combinations, and most securely detected, in the following way:—the substance supposed to contain an ammoniacal salt, either in the solid state or dissolved, is mixed with an excess of hydrate of lime in a small beaker, and, if necessary, a little water; if the substance supposed to contain an ammoniacal salt is in a state of solution, sufficient hydrate of lime must be added to the portion of solution examined for ammonia to render it perfectly dry and solid. The beaker is covered, after the mixing, with a glass plate, on the lower side of which adheres a small piece of moist turmeric or moist reddened litmus paper.

137. *Bichloride of platinum* ($PtCl_2$) produces in neutral and acid solutions of ammonia a yellow crystalline precipitate, which is a double salt of CHLORIDE OF AMMONIUM and CHLORIDE OF PLATINUM ($NH_4Cl, PtCl_2$).

138. Ammonia and its salts are distinguished from the fixed alkalies and their salts by being volatile (A 1). We have already noticed that ammonia is expelled from its aqueous solution on boiling the liquid; but salts of ammonia are not volatilized unless they are ignited in the dry state, for they are not expelled from their solutions by heat with one or two exceptions, and even these could not be volatilized with advantage in this way. Therefore to volatilize an ammoniacal salt we must ignite the dry substance in a crucible over a spirit or a gas lamp, until all fuming ceases. We must continue the ignition so long because the fumes are the volatilizing salt, and therefore, until they cease, all the ammoniacal salt is not expelled.

139. POTASH.—This alkali and its hydrate, when exposed to the air, absorb moisture and carbonic acid, the carbonate formed dissolving in the absorbed water. Almost all the salts of this base are readily soluble in water. They are colourless, provided the constituent acid be so. This alkali is an important constituent in many of our crystalline rocks; it exists there, in combination with SILICIC ACID, ALUMINA and IRON, as a double salt of SILICATE OF POTASH and SILICATE OF ALUMINA or IRON. The decay of these rocks is occasioned by the carbonic acid in the atmosphere decomposing the alkaline silicate. It is also found in the mineral kingdom as SULPHATE and NITRATE OF POTASH, the latter being *saltpetre*.

140. *Bitartrate of soda*[*] is a much more delicate test for potash than tartaric acid, because bitartrate of potash is soluble in acids, and an acid must be set free whenever tartaric acid is added to a solution containing a salt of potash. If the solution is acid, the free acid must be expelled, if practicable, by evaporation or ignition; or if not expelled, it must be neutralized with soda or carbonate of soda before testing for potash either with bitartrate of soda or tartaric acid. Bitartrate of soda cannot, of course, replace tartaric acid as a test for potash when the solution to be tested contains a free alkali, because bitartrate of potash is soluble in free alkalies; but if the other bases are sought for, the solution cannot be alkaline when we arrive at the examination for potash, and it is not often that we have to deal with an alkaline solution, even when the alkalies are the only bases that are examined for.

141. *Bichloride of platinum* produces, in neutral and acid solutions of potash, a yellow, crystalline precipitate,[†] a double

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[*] My friend, Mr. W. Plunkett, suggested the employment of bitartrate of soda. *See* 'Chemical Gazette,' vol. xvi, p. 217.

[†] Bichloride of platinum gives with iodine a dark-red colour; and as this colour prevents the yellow precipitate of bichloride of platinum and chloride of potassium from being distinctly seen, iodine should be expelled, if present, before testing for potash by this reagent. To expel it, evaporate to dryness with *concentrated nitric acid;* dissolve the residue in water, and add hydrochloric acid and bichloride of platinum, and then proceed in the usual way.

salt of CHLORIDE OF POTASSIUM and CHLORIDE OF PLATINUM (KCl, $PtCl_2$). The presence of free hydrochloric acid promotes the formation of this precipitate. It is slightly soluble in water, but wholly insoluble in alcohol. This is a very delicate test for potash or any of its compounds; the best method of applying it is to mix the solution under examination for potash with bichloride of platinum, evaporate to dryness upon a water bath, and treat the residue with alcohol, the excess of bichloride of platinum dissolves in the alcohol, colouring the solution yellow; the double salt of bichloride of platinum and chloride of potassium is left undissolved as a yellow, crystalline precipitate. The addition of bichloride of platinum should always be preceded by that of hydrochloric acid, to convert the potassium compound into the chloride, if it should not exist already in that form.

142. If a small particle of a potassium compound be introduced on the loop of a platinum wire (par. 78) into the melting space of the flame of a *Bunsen's gas-lamp* (pars. 64 and 65) or the inner flame of a spirit-lamp, it will, if volatile at the temperature of the flame (see pars. 66 to 72 and from 87) *colour* the part of the flame above the sample *blue-violet;* if the substance examined contains a sodium as well as a potassium compound the yellow colour imparted to the flame by the sodium compound overpowers and obscures the violet tint produced by the potassium one. But potash can be detected in the presence of soda (or lithia) if we look at the flame through deep blue cobalt glass;* through this coloured glass no coloured rays from soda (or lithia) can pass, but it admits those peculiar to potash. Potash, viewed through this coloured glass, gives to the flame an intense violet colour; and this is still visible when one part of potash is present with two hundred parts of soda. As all substances which make flame luminous, especially all organic substances which burn with separation of carbon give the same violet colour, these substances must

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* The cobalt blue glass can be obtained at the operative chemists. Before using the glass, it must first, of course, be ascertained how small a quantity of potash mixed with soda (or lithia) it will clearly indicate.

first be removed by heat, before the colour of the flame can be used as a test for potash.

143. The potash flame may be viewed through the indigo prism (par. 90) instead of the blue glass; the flame appears through the prism of *sky blue*, then *violet*, and at last of an intense *crimson red*, even when seen through the thickest layers of solution; admixtures of soda or lime do not hinder the reaction.

144. The potash flame viewed through the violet coloured glass (par. 92) appears violet and through the green coloured glass, blue-green.

145. The more volatile the salt, the more intense is the coloration it imparts to the flame; chloride of potassium and nitrate of potash volatilize rapidly, carbonate and sulphate less rapidly, and the phosphate still more slowly; but they all of them distinctly show the reaction, though decreasing in degree. The sensibility of the test may, in many cases, be increased by moistening the substance under examination with sulphuric acid, drying the substance at the border of the flame, and then introducing it into the melting space. With silicates and other difficultly volatile compounds of potassium, the reaction is best secured by fluxing it with pure gypsum in the melting space, there is formed a silicate of lime and volatile sulphate of potash which colours the flame. It is advisable to ignite decrepitating salts in a platinum spoon before attaching them to the loop of the platinum wire.

146. SODA.—This alkali and its hydrate, on exposure to the air, attract moisture and become fluid; but in absorbing carbonic acid from the air, which it does very rapidly, it again becomes solid. The salts of this base, with a few exceptions, are very soluble; the means we have of detecting it are therefore limited. It exists in the mineral kingdom as CHLORIDE (*kitchen salt*), SULPHATE (*Glauber's salt*), BORATE (*borax or tincal*), NITRATE and CARBONATE. It likewise forms a constituent of many SILICEOUS MINERALS.

147. If a small particle of a sodium compound be introduced, on the loop of a platinum wire, into the melting-space of the flame of a *Bunsen's gas lamp* or the inner flame of a spirit lamp,

it will, if volatile at the temperature of the flame, colour the part of the flame above the sample, intense yellow; this is the most characteristic test for sodium compounds. If the soda flame is made to illuminate a crystal of bichromate of potash, this salt appears perfectly colourless and transparent, and with an adamantine lustre. The following reaction is even more delicate. A piece of paper about a centimetre square is coated with red iodide of mercury, and placed upon a small holder *d* (fig. 1, page 18) which is moveable on an arm *c*, also moveable, attached to the chimney. When the least quantity of soda, sulphate of soda, or chloride of sodium is introduced into the melting space of the flame, the red iodide becomes white, with a faint tinge of fawn colour. The glaring contrast of these colours is apparent when the paper is lit up by being placed close to the red hot wire and bead, and the wire then placed in the flame, that the bead only reaches the melting space. Potash, lithia, and lime, cannot prevent this reaction.

148. The soda flame appears *orange* yellow, through the green glass (par. 92), even with the smallest quantities. This glass is particularly adapted to the recognition of soda in all its compounds (Merz).

149. Although the soda salts are a little less volatile than the potash salts, they display with regard to their relation, volatility, and the influence of sulphuric acid and pure gypsum in increasing their sensibility, the same behaviour as the potash ones; the student is therefore referred to par. 145 for further information.

150. *Antimoniate of potash* (KO, SbO_5) produces, in neutral or alkaline solutions of salts of soda, a white crystalline precipitate of ANTIMONIATE OF SODA (NaO, SbO_5). In concentrated solutions the precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Violent agitation of the fluid promotes the separation of the precipitate. Acid solutions decompose antimoniate of potash, antimonic acid being precipitated; free acids must therefore be first neutralized with potash before this test can

be applied. Antimoniate of soda is soluble in carbonate of potash; if this substance be present in the solution it must be nearly saturated with acetic acid.

151. The double chloride of bichloride of platinum and chloride of sodium is soluble in alcohol, and very soluble in water; therefore this reagent (bichloride of platinum) produces no insoluble compound with soda or any of its salts, either in an aqueous or alcoholic solution.

APPENDIX TO THE FIRST GROUP.

152. LITHIA (LiO).—The hydrate of this alkali is less soluble in water than the hydrates of potash and soda, and it does not deliquesce in the air. The salts of this base are colourless, provided the constituent acid be so. Most of its salts are soluble in water; the carbonate is rather sparingly soluble in that liquid; the solution of this salt has an alkaline reaction. Lithia occurs in certain minerals, particularly in spodumene, petalite, and lepidolite.

153. *Phosphate of soda* produces in not over-dilute solutions of lithia, upon boiling, a heavy white crystalline precipitate of basic phosphate of lithia; if the solution is then evaporated to dryness, and the residue treated with cold water, the basic phosphate remains undissolved. We can therefore in this way distinguish lithia from, and in the presence of, potash and soda.

154. "If a salt of lithia (more particularly chloride of lithium) is exposed on a platinum wire into the melting space of the flame of a Bunsen's gas-lamp, or the inner flame of a spirit-lamp, the outer flame shows a strong CARMINE tint. Presence of salts of soda (but not salts of potash) conceals this reaction."

155. If the lithium flame be viewed through the indigo prism, it appears through the thinnest layer of the indigo solution of a *carmine-red*, which, with increasing thickness of the solution, becomes *gradually feebler*, and *disappears* before the thickest layers pass before the eye: whereas the potassium

flame appears through the thinnest layer of the indigo solution of a *sky-blue*, then *violet*, and at last of an intense *crimson-red*, even when seen through the thickest layers of the solution. Admixtures of soda or lime do not hinder the reaction of either the lithium or potassium.

156. As, of all lithium compounds, the carbonate and chloride give the most intense coloured flame, it is only necessary to mark on the prism the place at which the lithia disappears, to obtain a space above this mark which transmits red potash rays, but never red lithia rays. As this part of the prism acts in the same way as a thick cobalt glass in detecting potash compounds in the presence of soda compounds, the cobalt glass can be dispensed with for determining potash.

157. Lithia with an admixture of potash is detected by bringing a sample into the melting-space, and comparing its flame with that of a sample of pure potash placed side by side with it in the melting-space. With thin layers of the solution, the lithia flame appears redder than the pure potash flame; with somewhat thicker layers the flames are equally red, if the proportion of lithia to potash be very small; if the lithia be in excess, the intensity of the red lithia flame sensibly diminishes with thicker layers, while the red flame of potash is scarcely weakened. In this manner a few thousandths of lithia may be detected in the presence of potash. Soda has almost no influence on the reaction.*

SECOND GROUP.

BARYTA. STRONTIA. LIME. MAGNESIA.

158. The members of this group are called alkaline earths. They are soluble in water in their pure (caustic) state, also as sulphides. Magnesia, however, is very sparingly soluble in water. Their solutions exhibit an alkaline reaction.

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* For the quantitative determination of the alkalies by the photochemical method see Appendix to Part I.

159. The metallic radicals of these oxides are *barium*, *strontium*, *calcium*, and *magnesium*, all of which decompose water at the ordinary temperature.

160. As magnesia differs so entirely from the other members of the group in its behaviour with reagents, it has not been included in the special table.

161. The group is subdivided; the first division comprising BARYTA, STRONTIA, and LIME; the second containing MAGNESIA. The members of the first subdivision are precipitated *completely* by CARBONATE OF AMMONIA, but magnesia is precipitated *only in part* by this reagent; and if any salt of ammonia, the acids of which form no insoluble compound with magnesia, is added to the solution containing the magnesia before adding the carbonate of ammonia, the carbonate of ammonia *will not cause the least precipitate* with the magnesia. If, therefore, we add to a solution which may contain the members of the second group chloride of ammonium and carbonate of ammonia—baryta, strontia, and lime, if they are present, will be precipitated as carbonates, whilst the magnesia will not be precipitated in the least degree. We generally add ammonia, after adding the chloride of ammonium, but before adding the carbonate of ammonia, to render the carbonate of ammonia we employ (if it is not) a neutral carbonate.

FIRST DIVISION.

162. When the student examines a solution even for the members of this division *only*, he must precipitate the baryta, strontia, and lime, by carbonate of ammonia, and precede the addition of this reagent by chloride of ammonium and ammonia.

163. The precipitate produced by the *general reagent*, carbonate of ammonia, must be dissolved in acetic acid, and the solution divided into two parts, which we shall call A and B.

164. Before we describe the way for separating the members of this division of the group, we shall propose six ques-

tions, which the student ought to solve by the aid of the table before he attempts the detection of baryta, strontia, and lime. 1st, Why are the precipitated carbonates directed to be dissolved in acetic acid; why not dissolve them in hydrochloric acid or nitric acid? 2nd, By what single reagent can we discover, in one operation, the absence of baryta and strontia? 3rd, How can lime be detected in the absence of the other two members? 4th, How can strontia be detected in the absence of baryta? 5th, Can lime be detected when strontia is present? 6th, Can strontia and lime be detected when baryta is present?

165. SULPHATE OF LIME precipitates baryta *immediately*, strontia *after the lapse of some time*, and lime *not at all* (*see* D 1, E 1, and F 1). One of the three cases will, therefore, occur on the addition of sulphate of lime to the A portion; either there will be no precipitate, or there will be one after the lapse of some time, or there will be an immediate one. If there is no precipitate, examine according to par. 166; if there is one after the lapse of some time, examine according to par. 167; if there is one immediately, examine according to par. 168.

166. If, in the A portion, a solution of *sulphate of lime* causes no precipitate, even after the lapse of some time, BARYTA and STRONTIA *are absent;* LIME must therefore be present*—as one of the members of a group must, at least, be present whenever a precipitate is obtained by the general reagent of that group.† As lime, in the form of sulphate, has been added to the A portion of the solution, we cannot in that portion discover whether it (lime) was originally present; we therefore confirm its presence by adding to the B portion ammonia and a solution of oxalate of ammonia (F 4).

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* If the previous group or groups have been fully precipitated before adding the carbonate of ammonia, or else they might—that is, the portion not precipitated—cause a precipitate with carbonate of ammonia.

† This statement must be read in the light of the above note.

TABLE II.

BEHAVIOUR OF THE SECOND GROUP WITH THE SPECIAL REAGENTS.

BARYTA (BaO).	STRONTIA (SrO).	LIME (CaO).
D 1. *Sulphate of lime,* (CaO, SO_3) in solution, precipitates baryta *immediately,* from its solutions, in the form of SULPHATE (BaO, SO_3) insoluble in acids and alkalies.	E 1. *Sulphate of lime,* in solution, precipitates strontia *after* the *lapse of some time,*[*] from its solutions, in the form of SULPHATE (SrO, SO_3), almost absolutely insoluble in acids and alkalies.	F 1. *Sulphate of lime* produces no precipitate in solutions of lime.
D 2. *Chromate of potash* (KO, CrO_3), in solution, produces, in neutral and alkaline solutions of baryta, a pale yellow precipitate of CHROMATE OF BARYTA ($Ba O, Cr O_3$), insoluble in the alkalies and acetic acid, soluble in hydrochloric and nitric acids.	E 2. *Chromate of potash,* in solution, causes, in concentrated solutions of salts of strontia, a bright yellow precipitate ($Sr O, CrO_3$), but not in dilute solutions, or such as contain *free acetic acid.*	F 2. *Chromate of potash,* in solution, produces no precipitate in solutions of lime, CHROMATE OF LIME being soluble.
D 3. *Sulphuric acid* and *the soluble sulphates* behave in the same manner in solutions of baryta as sulphate of lime.	E 3. *Sulphuric acid* and the *soluble sulphates* precipitate strontia completely from its solutions, in the form of SULPHATE. The precipitate will not appear immediately, unless the solution be very concentrated.	F 3. *Sulphuric acid* and the *alkaline sulphates* cause only in concentrated solutions of lime a partial precipitate of SULPHATE OF LIME, which redissolves completely in a large amount of water.
D 4. *Oxalic acid* ($HO, C_2O_3 = HO, \bar{O}$), in solution, produces only in concentrated solutions of baryta a white precipitate of Oxalate of Baryta ($BaO, \bar{O}$), soluble in acids. The addition of ammonia renders this reaction therefore more susceptible.	E 4. *Oxalic acid,* in solution, precipitates, even from dilute solutions of strontia, a white precipitate of Oxalate of Strontia. The addition of ammonia promotes the formation of the precipitate.	F 4. *Oxalic acid,* in solution, throws down from neutral solutions of lime, even if highly diluted, a precipitate of Oxalate of Lime. The addition of ammonia renders this reaction more delicate.

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[*] The formation of the precipitate is much promoted by agitation.

167. If, in the A portion, a solution of *sulphate of lime* produces a precipitate after the lapse of some time, BARYTA *is absent*, STRONTIA *is*, and LIME *may be, present.* The presence or absence of lime cannot be determined, as long as any strontia remains in solution; because the reagents, which precipitate lime, precipitate strontia also (E 3, F 3, E 4, F 4). We add, therefore, to the B portion *dilute sulphuric acid;* this acid precipitates all the strontia (E 3), and only a small portion of lime in a concentrated and none at all from a dilute solution (F 3); in any case, sufficient lime remains in solution for detection. Filter off from the precipitate produced by the sulphuric acid, after sufficient time (one or two hours) has been allowed for the precipitation of the sulphate of strontia, and add to the filtrate *ammonia* in excess and then *oxalate* of *ammonia*, which will cause a precipitate, if LIME is present.

168. If, in the A portion, a solution of *sulphate of lime* causes an immediate precipitate, BARYTA *is*, and STRONTIA and LIME *may be, present.* As sulphate of lime cannot be employed to detect strontia in the presence of baryta, and as baryta causes a precipitate with all the reagents which precipitate strontia and lime, the former must be got rid of before we can ascertain the absence or presence of the two latter substances. For this purpose, *chromate of potash* must be added to the B portion, which precipitates baryta only (D 2, E 2, F 2); filter, and to the filtrate* (which will be of a yellow colour, from the excess of chromate of potash, if the baryta has been completely precipitated) add *ammonia* in excess and *carbonate of ammonia*, and warm the solution; if a *precipitate is produced*, it may be due to the presence both of STRONTIA and LIME; if *no precipitate is produced*, STRONTIA and LIME *are absent.* If a precipitate is produced wash it until all excess of chromate of potash has been removed, then dissolve it in acetic acid, filter, if necessary, through a very small filter, and add to the clear solution not too small a quantity of the

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* It is absolutely necessary to have the filtrate from the chromate of baryta perfectly bright and transparent, which sometimes is troublesome to obtain. For the mode of securing it, see par. 40.

dilute solution of *sulphate of potash*,* after which addition, the solution must be well agitated; if the sulphate of potash produces a precipitate, after the lapse of some time, STRONTIA *is present*. If the sulphate of potash solution has produced a precipitate, add some dilute sulphuric acid to complete the precipitation, and allow sufficient time (one or two hours) for the complete separation of the sulphate of strontia before filtering; add to the filtrate, or to the solution, without filtering, if sulphate of potash has produced no precipitate, *ammonia in excess* and *oxalate of ammonia;* if this last reagent produces a precipitate, LIME is present.†

169. *The following precautions are to be attended to in the analysis of this group.*—The solution of sulphate of lime must be added in not too small a quantity, and it must always be added in the cold, as this reagent is less soluble in hot than cold water. Time must be allowed for the formation of the precipitate produced by this reagent in solutions of strontia, the formation of which is much promoted by agitation. In separating strontia from a solution by sulphate of potash, the liquid ought not to be filtered immediately, but a due time allowed for the complete separation of the precipitate from the solution; and the solution ought not to be warmed, owing to the less solubility of sulphate of lime in hot than cold water.

SPECIAL REMARKS.

170. BARYTA.—This oxide is of a grayish white colour; it combines with water, forming a hydrate (BaO, HO). Both

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* Care must be taken to make the solution of sulphate of potash of the strength directed in the list of reagents. Of that strength, it contains the same quantity of sulphuric acid as a saturated solution of sulphate of lime contains in a like quantity of liquid; it is, therefore, sufficiently strong to precipitate strontia, but not to precipitate lime.

† For another method for the separation and detection of these three substances, and for the photo-chemical method, the student is referred to par. 183.

the oxide and its hydrate are soluble in water. The solution reacts strongly alkaline, and when exposed to the air absorbs carbonic acid and becomes covered with a film of carbonate of baryta, the absorption continuing until all the baryta has been precipitated as carbonate.

171. The salts of baryta are colourless, provided the constituent acid be so. Most of them are insoluble in water; but they are all, with the exception of the sulphate, soluble in hydrochloric and nitric acid. The salts which are soluble in water do not affect vegetable colours, and are decomposed upon ignition, with the exception of chloride of barium. The SULPHATE (*heavy spar*) and the CARBONATE (*witherite*) are the principal minerals of this oxide.

172. *Hydrofluosilicic acid* (HF, SiF_2) throws down, both from neutral and alkaline solutions of baryta, a white precipitate of SILICOFLUORIDE OF BARIUM ($BaF, Si F_2$), which appears only after much agitation and the lapse of some time, in dilute solutions; it is perceptibly soluble in hydrochloric and in nitric acid. Addition of an equal volume of alcohol renders the precipitation rapid, and so complete that the filtrate remains clear upon addition of sulphuric acid.

173. If salts of baryta are held on the loop of a platinum wire in the hottest part of *Bunsen's gas flame*, the part of the flame above the sample is coloured YELLOWISH-GREEN; or if the baryta salts are held in the *inner spirit-blowpipe flame*, the same coloration is imparted to the part of the flame above the sample. With the soluble baryta salts, and also with the carbonate and sulphate of baryta, the reaction is immediate, or very soon; but the phosphate and also silicates decomposable by acids, demand previous moistening of the sample with sulphuric acid or hydrochloric acid, by which means the baryta may be detected by the flame coloration. Silicates which hydrochloric acid fails to decompose must be fluxed with carbonate of soda, when the carbonate of baryta produced will show the reaction. It is characteristic of the yellowish-green baryta coloration of the flame that it appears bluish-green

when viewed through the green glass (par. 92). If the sulphates are selected for the experiment, presence of lime and strontia will not interfere with the reaction.—*Fresenius.*

174. STRONTIA.—This oxide and its salts resemble, in their colour, solubility, and other properties, the corresponding compounds of baryta. The hydrate of this oxide is however less soluble in water than the hydrate of baryta. The SULPHATE (*celestine*) and the CARBONATE (*strontianite*) are the principal minerals of strontia.

175. *Hydrofluosilicic acid* causes no precipitate in solutions of strontia; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

176. The CHLORIDE and NITRATE of STRONTIA are soluble in alcohol; the corresponding salts of baryta are insoluble. If an alcoholic solution of either of these strontian salts be ignited, it will burn with a *beautiful crimson flame,* which becomes more apparent on stirring the solution.

177. If a small particle of a strontium compound be introduced on the loop of a platinum wire into the melting space of the flame of a *Bunsen's gas lamp*, or the inner flame of a spirit lamp, it will impart an *intensely red colour* to the flame. As chloride of strontium gives the most intense coloration of all the strontium compounds, it is advisable with all the other compounds, first to ignite them in the flame, then moisten with hydrochloric acid, and again to introduce them into the flame. "Viewed through the *blue glass* the strontia flame appears purple or rose (difference between strontia and lime, which latter body shows a faint greenish-gray colour when treated in this manner); this reaction is the most clearly apparent if the sample moistened with hydrochloric acid is let spirt up into the flame. In presence of baryta the strontia reaction shows only upon the first introduction into the flame of the sample moistened with hydrochloric acid."

178. LIME.—This oxide and its salts resemble in their general behaviour the corresponding compounds of baryta and strontia. The hydrate of lime is less soluble in water than the

hydrates of strontia or baryta; it is also more sparingly soluble in hot than cold water. The solution absorbs carbonic acid from the air, the lime becoming converted into carbonate. The principal minerals of lime are the SULPHATE (*gypsum*, *selenite* $CaO, SO_3 + 2\ aq$) and (*anhydrite* CaO, SO_3), the CARBONATE (*chalk*, *limestone*, *calcareous spar*), the double CARBONATE OF LIME and MAGNESIA (*dolomite*) $(CaO,CO_2)+3(MgO,CO_2)$, and the FLUORIDE OF CALCIUM (*fluor spar* CaF).

179. *Hydrofluosilicic acid* does not precipitate lime from its solutions.

180. CHLORIDE OF CALCIUM and NITRATE OF LIME are soluble in alcohol. The alcoholic solution of these salts, when ignited, burns with a *yellowish-red coloured flame.*

181. *Arsenite of ammonia* produces, in aqueous solutions of chloride of calcium, an immediate precipitate of ARSENITE OF LIME. In solutions of chloride of barium or strontium a precipitate is produced by this reagent only after the lapse of some time. Should this test be resorted to for confirming the presence of lime, ammoniacal salts (if present) must first of all be removed from the solution, because all the salts of arsenious acid which are insoluble in water dissolve in it if ammoniacal salts are present.

182. If a small particle of a calcium compound be introduced on the loop of a platinum wire into the melting space of the flame of a *Bunsen's gas-lamp*, or the inner flame of a spirit-lamp, it will impart an orange-red colour to the outer flame. As chloride of calcium gives, of all the calcium compounds, the most intense coloration, it is advisable with all the other compounds to moisten them with hydrochloric acid before introducing them into the flame. The coloration appears of a finch green colour when viewed through the green glass, whilst the strontia flame when viewed through the green glass appears only of a weak yellow. In presence of baryta the lime coloration shows only upon the first introduction of the substance into the flame.

183. Before describing the special properties of magnesia, we will give Fresenius's method for the separation and detection

of baryta, strontia, and lime (par. 184), and also the photochemical method (Par. 186).

184. "Dissolve the precipitate produced by the general reagent, carbonate of ammonia, after it has been well washed in the least possible amount of hydrochloric acid, and add to a small portion of the fluid some solution of *sulphate of lime,* (not too little); *a precipitate is formed immediately;*[*] this indicates BARYTA. Besides this, strontia and lime may also be present.

185. "Evaporate the remainder of the hydrochloric solution of the precipitate produced by carbonate of ammonia to dryness, digest the residue with strong alcohol, decant the fluid from the undissolved chloride of barium, dilute with an equal volume of water, mix with a few drops of hydrofluosilicic acid, which throws down the small portion of baryta that had dissolved in the form of chloride of barium. Allow the mixture to stand for some time; filter, evaporate the alcoholic solution to dryness, dissolve the residue in water, and test a portion of the fluid with a dilute solution of sulphate of potash. If a precipitate forms immediately, or in the course of half an hour, the presence of STRONTIA is demonstrated. In that case, let the fluid, with the precipitate in it, stand at rest for some time, then filter, and add ammonia and oxalate of ammonia to the filtrate. The formation of a white precipitate indicates LIME. If sulphate of potash has failed to produce a precipitate, the remainder of the solution of the residue left upon evaporation of the alcoholic fluid is tested at once with ammonia and oxalate of ammonia for lime.

186. "The three alkaline earths may be detected in mixtures containing all three of them by the different coloration which they severally impart to the flame. To this end the sample under examination is repeatedly moistened with sulphuric acid, then cautiously dried, and introduced into the fusion zone of

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[*] If a precipitate is not formed immediately, but only after the lapse of some time, examine the other portion of the solution according to 167; if no precipitate is formed, examine the other portion of the solution according to 166.

the gas flame. After the evaporation of the alkalies that may chance to be present, the baryta coloration will make its appearance alone. After this coloration has completely disappeared, and the sample moistened with hydrochloric acid gives on spirting no longer a flame coloration of a bluish-green tint when viewed through the green glass, the sample is moistened again with hydrochloric acid, and tested for lime by viewing it through the green glass when spirting, for strontia by viewing it under the same circumstances through the blue glass."—*Fresenius.*

187. MAGNESIA.—This oxide differs from the other members of this group, not only by its non-precipitation by *carbonate of ammonia* in the presence of *ammoniacal salts*, but likewise from the difficult solubility of its hydrate and the ready solubility of its sulphate. The oxalate and chromate, as well as some other salts of magnesia, are soluble in water. The soluble magnesian salts have a nauseous bitter taste; they do not alter vegetable colours when in a neutral state, and, with the exception of sulphate of magnesia, they undergo decomposition when ignited. All the salts of magnesia which are insoluble in water dissolve readily in hydrochloric acid. Magnesia is found in the mineral kingdom principally in the state of SULPHATE (*Epsom salts* MgO, SO_3+HO+6 aq), of CARBONATE, and in combination with SILICIC ACID in various proportions, forming the *meerschaum*, *serpentine*, &c.

188. *Ammonia* precipitates from aqueous solutions of salts of magnesia a portion as HYDRATE (MgO, HO). The rest of the magnesia remains in solution, with the salt of ammonia formed, as a double salt. The presence of salts of ammonia prevents the precipitation altogether.

189. The *fixed alkalies* and the other *alkaline earths* precipitate magnesia from its solutions in the form of HYDRATE. This precipitate is soluble in salts of ammonia; the addition therefore of these substances, either before or after the precipitation, prevents or redissolves the precipitate formed.

190. *Arseniate of ammonia* ($3\ NH_4O, AsO_5$) produces, in solutions of magnesia, a white precipitate of ARSENIATE OF

MAGNESIA and AMMONIA ($2\ MgO, NH_4O, As\ O_5$), which is soluble in acetic and other weak acids.

191. *Phosphate of soda* ($2\ NaO, HO, PO_5$) produces, in concentrated solutions of magnesia, a precipitate of PHOSPHATE OF MAGNESIA ($2\ MgO, HO, PO_5$). A magnesian phosphate more insoluble in water may be produced by adding, along with the *phosphate of soda, chloride of ammonium and ammonia*; the precipitate in this case being PHOSPHATE OF MAGNESIA AND AMMONIA ($2\ MgO, NH_4O, PO_5$); both phosphates are soluble in free acids.

192. Phosphates of magnesia and ammonia, and arseniate of magnesia and ammonia, are the only magnesian salts which are insoluble in aqueous solutions containing salts of ammonia.

193. If magnesia or any of its compounds, after being ignited strongly by the blowpipe flame upon a charcoal support, be moistened with *nitrate of cobalt*, and again ignited, the mass assumes, on cooling, *a pale flesh colour.*

194. Salts of magnesia impart no colour to the flame.

THIRD GROUP.

OXIDE OF ZINC. OXIDE OF MANGANESE. OXIDE OF NICKEL. OXIDE OF COBALT.

195. The members of this group are insoluble in water; but they dissolve readily in the dilute mineral acids, sulphuric, nitric, and hydrochloric acids, the salts they form with these acids being soluble. They are not precipitated in the least degree from their solutions by hydrosulphuric acid, if a free mineral acid is present. They are not precipitated completely from their neutral solutions by hydrosulphuric acid, but they are completely precipitated by that acid from their alkaline solutions in the state of sulphides. Their sulphides are insoluble in the alkalies and alkaline sulphides, with the exception of sulphide of nickel, which, under certain circumstances, dissolves to a slight extent in the alkaline sulphides, imparting thereby to the solution a brownish colour.

196. *Carbonate of baryta* does not precipitate the oxides of this group from the aqueous solutions of their salts, with the exception of their sulphates, when this reagent is digested in their solutions at the *common temperature.*

197. The metallic radicals of these oxides possess the following properties: *manganese* decomposes water at 212° Fahr., and *zinc, nickel,* and *cobalt,* decompose it at a red heat, and at common temperatures in contact with strong acids.

198. The precipitate produced by the general reagent, sulphide of ammonium, after being well washed with water containing a little sulphide of ammonium must be examined if it is of a *light colour* according to par. 199; if it is of *black colour* according to par. 200.

199. The precipitate is of a *light colour;* NICKEL and COBALT must therefore be absent (J1, K1). Examine the precipitate for MANGANESE by the blowpipe test (207); if manganese is *absent,* examine the precipitate for ZINC by the blowpipe test (209). *When manganese is present* dissolve the precipitate in as small a quantity of *boiling dilute hydrochloric acid* as possible;* boil to expel sulphuretted hydrogen,† then add *carbonate of ammonia* in excess and boil for some time: the manganese will be precipitated as carbonate (G 3), whilst ZINC, if present, will remain in solution. Filter, and to the filtrate add *sulphide of ammonium*—when zinc, if present, will be precipitated as sulphide; confirm its presence by examining the precipitate by the blowpipe test.

200. The precipitate is *black;* all the members of the group must therefore be sought for. Examine a portion of the precipitate for MANGANESE by the blowpipe test. Treat the rest

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* In order to use as little acid as possible, pour the boiling acid in small quantities at a time upon the precipitate collected upon the filter. If the precipitate be very large remove it from the filter into an evaporating dish before adding the acid.

† To ascertain when all the sulphide of hydrogen is expelled, hold a piece of bibulous paper, moistened with a solution of some soluble salt of lead, over the boiling liquid; when the lead paper does not alter in colour, all the sulphide of hydrogen is expelled.

of the precipitate, whether manganese is present or not, with *cold dilute hydrochloric acid;* the sulphides of nickel and cobalt will remain undissolved, whilst the sulphides of manganese and zinc will dissolve; examine the acid solution according to par. 201, and the undissolved portion according to par. 202.

201. Boil the filtered hydrochloric acid solution, which may contain MANGANESE and ZINC, until all *sulphide of hydrogen* is expelled (see second note, page 75), then add a solution of one of the *fixed alkalies in excess;* manganese* will be precipitated, whilst zinc will remain in solution; filter if the alkali has produced any precipitate, and add to the filtrate or to the solution (when it does not require filtering) sulphide of hydrogen, when zinc, if present, will be precipitated.

202. After having washed the black residue, examine

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* It is almost impossible to prevent a minute quantity of the sulphides of cobalt and nickel oxidizing, even if the precipitate is washed most carefully with water containing sulphide of ammonium; the oxidized portion of these two bodies will, therefore, be present in the hydrochloric acid solution, and consequently be precipitated by the fixed alkali; a precipitate may, therefore, be produced by the alkali, when no manganese is present. It will not be necessary to examine this precipitate for nickel and cobalt, as sufficient will remain undissolved, unless the student has allowed the sulphide of ammonium precipitate to remain on the filter for a great length of time.

Potash and soda solutions very frequently blacken slightly on the addition of sulphuretted hydrogen from their containing small traces of iron and copper; it is therefore necessary before employing the alkali solution to examine it for these metals; if one or both of them are present the precipitate produced by sulphuretted hydrogen must be redissolved in a few drops of dilute nitric acid, and if copper as well as iron is present sulphuretted hydrogen must be passed through the solution until it is in excess, the liquid must then be filtered, and the filtrate boiled in an evaporating dish with a few drops of nitric acid until all the sulphuretted hydrogen is expelled and the iron has become peroxidized, ammonia is then added in excess, the liquid filtered, and to the filtrate must be added sulphide of ammonium, which will produce a white precipitate if zinc is present. If the alkali solution does not contain copper but only iron after the solution of the precipitate in nitric acid, ammonia is at once to be added in excess, and the filtrate from the ammonia precipitate tested for zinc with sulphide of ammonium.

it for nickel and cobalt in the following way:—Expose a small portion of the precipitate on a bead of borax to the outer blowpipe flame, in the way directed in par. 212.* A blue bead denotes the presence of cobalt; this is a safe and certain test for cobalt; consequently, if a blue bead is not produced, cobalt is absent. If a yellow, and not a blue bead has been formed, which becomes gray and dull in the inner flame, nickel is present. When cobalt is present, nickel is sought for in the following way:—The remainder of the precipitate is dissolved in nitro-hydrochloric acid, and the acid solution evaporated almost to dryness; a concentrated solution of cyanide of potassium is then added in excess, and the whole solution must then be boiled for some time, adding a little water from time to time, to replace that which evaporates. To the solution, which must not be filtered even if a precipitate has been formed, is added, when it is cold, sulphuric acid slightly in excess; if in some hours after the acid has been added a precipitate appears, nickel is present; if no precipitate appear, or at least only a crystalline one which redissolves in water, nickel is absent.

203. Nickel may also be detected in the presence of cobalt by the two following methods. 1st method:—"The acid solution which contains cobalt and which may contain nickel, must be evaporated nearly to dryness, nitrite of potash must then be added in not too small a proportion, then acetic acid to strongly acid reaction, then let the mixture stand for at least several hours in a moderately warm place, when cobalt will separate as nitrate of sesquioxide of cobalt and potash; the nickel may then be readily precipitated from the filtrate by soda or sulphide of ammonium. 2nd method:—Saturate with chlorine the very dilute solution of the two metals in hydrochloric acid, having the acid slightly in excess; add carbonate of baryta in excess, and let the fluid stand twenty-four hours. The cobalt is entirely precipitated in this process as black sesquioxide, whilst the nickel remains in solution, and may, after the removal of

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* Consult par. 79.

the baryta by sulphuric acid, be thrown down with solution of soda."*

204. *The following precautions are to be attended to in the analysis of this group:*—When manganese is present, care must be taken to expel all the sulphuretted hydrogen from the hydrochloric acid solution, before carbonate of ammonia is added to separate the manganese from the zinc. Before adding sulphuric acid to the cyanide of potassium solution, it will be better to add a little water, in order to prevent any sulphate of potash from crystallizing out, which might mislead the student as regards nickel. On adding caustic soda to the hydrochloric acid solution, which may contain the oxides of zinc and manganese and small traces of the oxides of nickel and cobalt, from the partial oxidation of their sulphides, a small precipitate will frequently be formed, if only zinc be present. This is occasioned by the caustic alkali having absorbed some carbonic acid from the air, and become partially converted into carbonate which causes a partial precipitation of the zinc.

SPECIAL REMARKS.

205. PROTOXIDE OF MANGANESE.—Numerous oxides of manganese exist as natural productions, and a still larger number can be formed artificially. The only one treated of in this work is the first or lowest compound of oxygen with manganese. All the others are reduced to this state by adding to their solutions hydrosulphuric acid, or any other reducing agent. This oxide is of a greenish gray colour, and its hydrate is white. Both, however, turn brown when exposed to the air, being converted into higher oxides. Its salts are colourless or of a pale red; the solutions of those soluble in water do not affect vegetable colours; and the salts soluble in water are readily decomposed at a red heat, with the exception of the sulphate. The most abundant source of manganese

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* The student ought to state all the different methods which could be adopted for the separation of the members of this group.

TABLE III.

UR OF THE THIRD GROUP WITH THE SPECIAL REAGENTS.

OXIDE OF MANGANESE (MnO).	OXIDE OF ZINC (ZnO).	OXIDE OF COBALT (CoO).	OXIDE OF NICKEL (NiO).
G 1. Sulphide of Manganese (MnS) is *flesh-coloured*, but becomes *brown* on exposure to the air. It is soluble in the weak acids, as acetic, as well as in the dilute mineral acids.	H 1. Sulphide of Zinc (ZnS), like the oxide, is white. It is insoluble in acetic acid, but dissolves in the dilute mineral acids.	I 1. Sulphide of Cobalt (CoS) is *black*. It is insoluble in the dilute mineral acids, as well as in the weaker acids. It is soluble in Nitro-hydrochloric acid.	K 1. Sulphide of Nickel (NiS) is *black*. It is insoluble in the dilute mineral acids, as well as in the weaker acids. It is soluble in Nitro-hydrochloric acid.
G 2. The *fixed alkalies* precipitate from solutions of this Oxide (MnO) the HYDRATE, which is of a whitish colour at first, but speedily becomes blackish brown on exposure to the air. *The Hydrate is insoluble in an excess of either of the fixed alkalies.* The presence of ammoniacal salts prevents in a great measure the precipitation.	H 2. The *fixed alkalies* precipitate from solutions of this oxide (ZnO) the HYDRATE, which is white. *The Hydrate of this oxide is completely soluble in an excess of either of the fixed alkalies, if it (the alkali) is perfectly free from carbonic acid.*	I 2. The *fixed alkalies* produce in solutions of this oxide (CoO) *blue* precipitates of *basic salts of Cobalt*, which turn *green* on exposure to the air; and are converted, upon boiling, into the PALE RED HYDRATE of this oxide, which is generally discoloured, owing to a little $Co\ O_3$ being formed. *Each of these precipitates is insoluble in an excess of either of the fixed alkalies.*	K 2. The *fixed alkalies* precipitate from solutions of this oxide (NiO) the HYDRATE, in the form of a *light green precipitate*, which is unalterable in the air, and *insoluble in an excess of either of the fixed alkalies.*
G 3. *Carbonate of Ammonia* produces in solutions of this Oxide a precipitate of the *Carbonate* ($Mn\ O, CO_2$), which is white, *and insoluble in an excess of the reagent*, especially on boiling.	H 3. *Carbonate of Ammonia* produces in solutions of this oxide a precipitate of *white* BASIC CARBONATE OF ZINC, which is easily soluble in an excess of the reagent.	I 3. *Carbonate of Ammonia* produces in solutions of this oxide a *red* precipitate of CARBONATE OF COBALT, which is *readily soluble in an excess of the reagent*, the solution having a red colour.	K 3. *Carbonate of Ammonia* produces in solutions of this oxide an *apple-green* precipitate of *Carbonate of Nickel*, which is *readily soluble in an excess of the reagent*, the solution having a greenish blue colour.

The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, &c.

is the PEROXIDE (MnO_2), which exists in nature under a variety of forms.

206. Ammonia precipitates this oxide (MnO) in part from its solutions as hydrate, which an excess of the reagent does not redissolve. But ammonia in the presence of chloride of ammonium, or in fact any salt of ammonia, the acid of which causes no insoluble compound with manganese, causes no precipitate in solutions of manganese. An ammoniacal solution of manganese attracts oxygen from the air, which converts the manganese oxide into a higher oxide; and this latter oxide being insoluble in ammonia, is deposited, as it becomes formed, in brownish flocks.

207. The smallest quantity of manganese can be detected in any of its compounds, by fusing them, in conjunction with carbonate of soda and a small quantity of nitrate of potash, upon platinum foil or wire, in the outer blowpipe flame; manganate of soda (NaO, MnO_3), which is of a bluish green colour, being produced.* "This method fails to detect manganese in limestone rocks, on account of the insolubility of the lime salt in carbonate of soda and nitrate of potash; but if, along with the two reagents just mentioned, a little borax be added, so as to attack and dissolve a portion of the mass, the well-known greenish blue enamel is quickly produced."—*Chapman.*

208. OXIDE OF ZINC.—The colour of this oxide is white, but it becomes yellow on being heated, regaining its original colour on cooling. The salts of zinc are colourless. The neutral ones, which are soluble in water, redden litmus paper and are decomposed by heat. The principal minerals of this metal are the anhydrous CARBONATE (calamine, ZnO, CO_2) and the SULPHIDE (Zinc blende ZnS).

209. When compounds of zinc, mixed with carbonate of soda, are subjected upon a charcoal support to the inner blowpipe flame, metallic zinc is produced, which volatilizes, and, on passing through the oxidizing flame, becomes again converted

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* Consult pars. 55 to 64, and also pars. 77 and 78.

into oxide. The charcoal support becomes encrusted with this oxide, which is of a yellow colour while hot, and turns white on cooling.*

210. If a compound of zinc be moistened with protonitrate of cobalt and exposed on charcoal to the outer blowpipe flame, a mass of a beautiful green colour will be produced; the colour is best seen when the mass has become cold.*

211. OXIDE OF COBALT.—The colour of this oxide is greenish-gray, its hydrate being pale red. Salts of cobalt are red when they contain water of crystallization; in the anhydrous state they are blue. Their solutions are red; yet when concentrated, or when they contain a free acid, they are blue or green, but they become green simply by the addition of water. The solutions of the neutral salts that are soluble in water redden litmus paper, and are decomposed by heat. The principal mineral of this metal is the BRIGHT WHITE COBALT ($Co\ As_2 + Co\ S_2$).

212. Ammonia produces in solutions of this oxide the same precipitate as the fixed alkalies do; but the precipitate is soluble in an excess of ammonia, the ammoniacal solution having a reddish-brown colour: the fixed alkalies produce no precipitate, or at least a very slight one, in an ammoniacal solution of protoxide of cobalt. Ammonia fails to precipitate oxide of cobalt from its solutions, if chloride of ammonium is present.

213. Cyanide of potassium ($KC_2N = KCy$) precipitates from *acid* solutions of cobalt salts a brownish-white cyanide of cobalt, $Co\ Cy$, dissolving easily in an excess of the precipitant: from which solution the cyanide of cobalt cannot be again precipitated by acids, as it exists now in the form of cobalticyanide of potassium, $K_3\ Co_2\ Cy_6$.

$$2\ Co\ Cy + 3\ KCy + H\ Cy = K_3\ Co_2\ Cy_6 + H.$$

214. "If the salt of cobalt contains nickel, the addition of

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* Before performing these blowpipe operations consult pars. 74 and 75.

hydrochloric acid to the solution of the cyanides produces a greenish precipitate, which always contains the whole of the nickel, and under particular circumstances all the cobalt—that is, when these two metals are in the proportion of three equivalents of nickel to two equivalents of cobalt. The precipitate consists then of cobalticyanide of nickel, $Ni_3Co_2Cy_6$. In case of a larger proportion of nickel, the precipitated cyanide of nickel is mixed with the former compound; but if the proportion of nickel is smaller, a part of the cobalt remains in solution as cobalticyanide of potassium."—*Will.*

215. "If *nitrite of potash* is added in not too small proportion to a solution of pròtoxide of cobalt, then acetic acid to *strongly* acid reaction, and the mixture put in a moderately warm place, all the cobalt separates, from concentrated solutions immediately or very soon, from dilute solutions after some time, as NITRITE OF SESQUIOXIDE OF COBALT AND POTASH ($Co_2\ O_3$, 3 KO, 5 NO_3, 2 HO), in the form of a crystalline precipitate of a beautiful yellow colour. The precipitate is only sparingly soluble in pure water, and altogether insoluble in saline solutions and in alcohol. When boiled with water it dissolves, though not copiously, to a red fluid, which remains clear upon cooling, and from which alkalies throw down hydrate of protoxide of cobalt. (Fischer, Aug, Stromeyer.) This excellent reaction enables us to distinguish nickel from cobalt. It is always necessary to concentrate the solution of protoxide of cobalt to a considerable extent before adding the nitrite of potash."—*Fresenius.*

216. The compounds of cobalt fused with borax in the loop of a platinum wire, in either flame of the blowpipe, produce a beautiful blue glass, which is a very delicate and characteristic test for cobalt. The cobalt compound must be used in very small proportion.*

217. OXIDE OF NICKEL.—The colour of this oxide is gray, its hydrate is green. Its salts likewise exhibit this latter colour, except when anhydrous; in this state they are mostly

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* Before making the blowpipe experiment consult pars. 77, 78, and 79.

yellow. The solutions of the neutral salts, which are soluble in water, redden litmus paper, and are decomposed at a red heat. The principal minerals of this metal are the ARSENICAL NICKEL (Ni As) and the NICKEL GLANCE ($Ni\ S_2+Ni\ As_2$).

218. Ammonia, added in small quantity to solutions of this oxide, produces in them a trifling greenish turbidity; upon further addition of the reagent, this redissolves readily to a blue fluid, containing a compound of oxide of nickel and ammonia.

219. Cyanide of potassium throws down from solutions of nickel a yellowish green precipitate of cyanide of nickel (Ni Cy), which redissolves in an excess of the precipitant as a double salt of cyanide of nickel, and cyanide of potassium (Ni Cy+K Cy); the solution is brownish-yellow. On the addition of hydrochloric or sulphuric acid to a solution of this double salt, the cyanide of nickel is reprecipitated, whilst the cyanide of potassium is decomposed, hydrocyanic acid being evolved; the cyanide of nickel is very difficultly soluble in an excess of either of the acids in the cold, but more readily upon boiling.

220. "*Nitrite of potash*, used in conjunction with acetic acid, fails to precipitate nickel even in concentrated solutions."

221. In the exterior flame of the blowpipe, oxide of nickel and its compounds impart to beads of borax a reddish-yellow tint; the colour fades upon cooling, and finally disappears almost entirely. If exposed with borax to the inner flame, the bead becomes gray; if a minute fragment of nitrate of potash be added to the bead after exposure to the inner flame, and it is then fused in the outer flame, it acquires a rich purple colour.*

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* Before making the blowpipe experiment consult pars. 77, 78, and 79.

FOURTH GROUP.

ALUMINA, SESQUIOXIDE OF CHROMIUM, SESQUIOXIDE OF IRON, PROTOXIDE OF IRON.

The PHOSPHATES OF ALUMINA, CHROMIUM AND IRON. THE PHOSPHATES OF THE ALKALINE EARTHS. The OXALATES OF BARYTA, STRONTIA AND LIME.*

APPENDIX TO THE GROUP.

TITANIC ACID. SESQUIOXIDE OF URANIUM.

222. The members of this group are insoluble in water, but they dissolve readily in the dilute mineral acids; after ignition, however, they dissolve with great difficulty, even in the concentrated mineral acids.

223. The metallic radicals of these oxides decompose water at a red heat, and at common temperatures in contact with strong acids.

224. Sulphide of ammonium precipitates the members of this group: it precipitates alumina and sesquioxide of chromium as oxides, for sulphide of aluminum and sulphide of chromium cannot be formed in the humid way; they (the sulphides) are decomposed by water into the oxides of the

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* The phosphates and oxalates do not engage the attention of the student as he passes through the basic groups; he has therefore only to deal with the substances given in Table IV. It is not until he has had some practice in examining both for acids and bases that the insoluble salts which are precipitated along with the oxides of this group are included in the course; the precipitate is then examined according to Table V.

The substances in the different appendices do not form a part of the course; they are, therefore, not included in the tables.

metals and hydrosulphuric acid. It is, therefore, the ammonia in the sulphide of ammonium which determines the precipitation of these two substances; consequently hydrosulphuric acid is always evolved when sulphide of ammonium is added to a solution containing either or both these substances. Protosulphide of iron is always formed when sulphide of ammonium is added either to a solution of a per- or proto- salt of iron, as a persulphide of iron is not formed in the humid way. Protosulphide of iron is of a black colour; it oxidizes rapidly on exposure to the air, which causes its colour to change from black to brown.

225. Peroxide of iron, and alumina are completely precipitated from the solutions of their salts *even in the cold*, by digesting in the solutions finely powdered carbonate of baryta; they are precipitated as hydrates mixed with basic salts of the oxides. Sesquioxide of chromium is also precipitated from its solutions by digesting carbonate of baryta in them; but the precipitation takes place in the cold only after long-continued digesting. Carbonate of baryta does not precipitate the protoxide of iron from the solution of its salts, with the exception of the sulphate, when it is digested in the solutions at the common temperature.

226. The precipitate produced by the general reagent, ammonia, after being well washed to free it from all foreign substances, must be examined for the *different members* composing the group and *also for manganese*, as this substance precipitates in small quantities along with the members of this group owing to its becoming converted into a higher oxide, the cause of which is explained in par. 206. We shall describe two methods for the examination of this group, the first is probably the best when iron or manganese is present. Before commencing the analysis of the precipitate according to either method the original solution must be tested for both oxides of iron, if it has not been done before. For this purpose, add to a portion of the original solution *ferrocyanide of potassium*, if a blue colour is produced by it, PEROXIDE OF IRON is present; add to another portion of the original solution *ferricyanide of potassium*, if this reagent also produces

a blue colour, PROTOXIDE OF IRON *is present*; consult par. 246 before testing with the ferro- and ferri- cyanide of potassium.

227. A small portion of the precipitate produced by ammonia must be examined for manganese by the blowpipe test (par. 207). The rest of the precipitate must be examined by one of the two following methods:

228. *1st Method.*—Fuse* the precipitate with equal parts of *carbonate of soda* and *nitrate of soda*† *or potash* in a porcelain crucible; after the fusion, allow the mass to cool, and then boil it with water and filter. If much chromium is present the filtrate will have a *yellow colour;* divide the filtrate into two portions; acidulate one of the portions with *acetic acid*, then add *acetate of lead*, if a *yellow* precipitate (chromate of lead) is produced‡ SESQUIOXIDE OF CHROMIUM is present in the substance under examination. Acidulate the other portion of the solution with *hydrochloric acid*, add *ammonia* in excess and then warm the solution, if no precipitate should appear on warming it allow it to stand for a short time (half an hour), if no precipitate should appear after allowing it to stand, ALUMINA *is absent.*

229. *2nd method.*—Dissolve the prceipitate in as small a quantity of boiling dilute hydrochloric acid as possible;§ add to this acid solution when cold, a cold solution of soda or potash which will precipitate the IRON as peroxide (N 3) *if present;*|| filter when a precipitate is produced and examine the *precipitate* according to par. 230, and boil the *filtrate*, or the solution which gave no precipitate to the fixed alkali, in a

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* See Fusion, page 14.

† About one part of the precipitate to two carbonate of soda and two of nitre.

‡ The carbonate of soda employed in the fusion must be entirely free from sulphate of soda, otherwise, on the addition of acetate of lead, a white precipitate of sulphate of lead will be found, which the student might mistake for chromate of lead.

§ See Precautions, par. 232.

|| Manganese if present will also be precipitated by the soda or potash solution, so that a precipitate may be produced by the alkali when peroxide of iron is absent.

dish for a considerable time, if a precipitate is produced by the boiling, SESQUIOXIDE OF CHROMIUM *is present* (see par. 231); filter when a precipitate is produced, and add to the filtrate, or to the solution which has failed to give a precipitate, hydrochloric acid until the solution is acid, then add *one grain* of *chlorate of potash*, and warm the solution so as to destroy all organic matter (note 2, page 89); add, lastly, ammonia in excess, and again warm the solution, if no precipitate should appear on warming it, allow it to stand for a short time (half an hour), if no precipitate should appear after allowing it to stand, ALUMINA *is absent*.

230. When a large quantity of peroxide of iron and only a small quantity of sesquioxide of chromium is present, all the chromium may be precipitated with the iron (see par. 239); if, therefore, sesquioxide of chromium should not be detected in the filtrate from the peroxide of iron precipitate, the iron precipitate ought to be fused with carbonate of soda and nitrate of potash or soda, and the fused mass treated with water and filtered, and the filtrate tested for CHROMIUM by acidulating it with acetic acid and then adding acetate of lead, if a yellow precipitate is produced SESQUIOXIDE OF CHROMIUM is *present*. It must also be remembered by the student that if a large quantity of sesquioxide of chromium and only a small quantity of iron is present, the iron may dissolve along with the sesquioxide of chromium in the caustic soda (see par. 239).

231. The precipitation of sesquioxide of chromium from its solution in the caustic alkali by boiling cannot be relied upon, as the presence of fixed organic matter completely prevents the precipitation. It is better, therefore, to add to the alkaline solution which may contain sesquioxide of chromium, peroxide of lead in excess (par. 237) and boil for some time, then filter, and add to the filtrate *acetic acid in excess*, if a yellow precipitate (chromate of lead) is produced sesquioxide of chromium was present in the solution; add to the filtrate from the chromate of lead, or to the solution which yields no precipitate of chromate of lead, sulphide of hydrogen to precipitate any lead

which remains in solution, filter, and to the filtrate add *one grain of chlorate* of potash and a small quantity of hydrochloric acid and warm the solution, add, lastly, ammonia in excess and again warm the solution, if no precipitate should appear on warming it, allow it to stand for a short time (half an hour), if no precipitate should appear after the lapse of that time ALUMINA *is absent.*

232. *The following precautions are to be attended to in the analysis of this group* :—Before dissolving the precipitate produced by ammonia, it must be completely freed, by washing it with distilled water, from all traces of ammonia. Dissolve the precipitate in as little acid as possible; for this purpose, pour the acid, in small quantities at a time, in a boiling state, upon the precipitate collected upon the filter. If the precipitate be very large remove it from the filter into an evaporating dish, before adding the acid. The precipitate produced by the soda solution in the cold, must be examined for iron, as it might be due to manganese, which was precipitated by ammonia, and which, like iron, is insoluble in the fixed alkalies.

SPECIAL REMARKS.

233. ALUMINA.—This substance is very abundant in nature. It forms not only the basis of common clay, but is likewise a principal ingredient in many of the precious stones. Along with slight traces of silica and peroxide of iron, it forms the CORUNDUM, SAPPHIRE, RUBY, DIAMANT SPAR, &c. As hydrate, it is known under the names of DIASPORE and GIBBSITE. Combined with silica and glucina, it forms the EMERALD, BERYL, EUCLASE, and CHRYSOBERYL. When pure, it is white; but it frequently possesses a yellowish tint when obtained by drying the hydrate. Its salts are colourless; the soluble ones redden litmus paper, and lose their acids upon ignition. "The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds of alumina; the compounds of alumina which are insoluble in hydrochloric

TABLE IV.

BEHAVIOUR OF THE FOURTH GROUP WITH THE SPECIAL REAGENTS.

ALUMINA (Al_2O_3).	OXIDE OF CHROMIUM (Cr_2O_3).	SESQUIOXIDE OF IRON (Fe_2O_3).	PROTOXIDE OF IRON (FeO).
L. 1. This oxide and its hydrate (Al_2O_3, $3HO$) are *white*.	M. 1. This oxide is green, and its hydrate (Cr_2O_3, $3HO$) a *bluish green powder*.	N. 1. This oxide and its hydrate are of a *reddish brown* colour.	O. 1. This oxide is *black*, and its hydrate is *white*.
L. 2. *Ammonia even* in the presence of its salts, precipitates Alumina in the form of HYDRATE, which an excess of the reagent *does not* redissolve.	M. 2. *Ammonia, even* in the presence of its salts. precipitates this oxide in the state of HYDRATE, which an excess of the reagent *does not* redissolve.	N. 2. *Ammonia even* in the presence of its salts, precipitates this oxide from its solutions in the form of HYDRATE (Fe_2O_3, $3HO$), which an excess of the reagent *does not* redissolve.	O. 2. *Ammonia, but not* in the presence of its salts, precipitates the HYDRATED PROTOXIDE (FeO, HO) from solutions of the protosalts of iron, which an excess of the reagent *does not* redissolve.
L. 3. The *fixed Alkalies* throw down Alumina from its solutions in the form of HYDRATE, which is *soluble* in an excess of reagent, from which solution it may be again precipitated on the addition of *Chloride of Ammonium*.	M. 3. The *fixed Alkalies* throw down from solutions of this oxide the HYDRATE, which is *soluble* in an excess of the reagent in the *cold*; but on *boiling* the solution, it is again precipitated.	N. 3. *The fixed Alkalies* precipitate from solutions of this oxide the HYDRATE, *insoluble* in an excess of the reagent	O. 3. The *fixed Alkalies* precipitate from solutions of this oxide the HYDRATE, *insoluble* in an excess of the reagent.
L. 4. *Carbonate of Ammonia* precipitates from solutions of Alumina the HYDRATE. This precipitation is attended with an evolution of carbonic acid.	M. 4. *Carbonate of Ammonia* precipitates from solutions of this oxide the HYDRATE, carbonic acid being given off.	N. 4. *Carbonate of Ammonia* precipitates from solutions of this oxide the HYDRATE, carbonic acid being given off.	O. 4. *Carbonate of Ammonia* precipitates from solutions of this oxide the PROTOCARBONATE (FeO, CO_2), soluble in chloride of ammonium.

1. The fixed alkaline carbonates throw down from their solutions all the members of this group, some as oxides, the rest as carbonates. An excess of the reagent does not redissolve the precipitate.
2. The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, &c.

acid are decomposed by ignition with carbonate of soda or bisulphate of potash" (*Fresenius*). The SULPHIDE OF ALUMINUM cannot exist in contact with water, being decomposed into alumina and hydrosulphuric acid.

234. If alumina or any of its compounds be ignited upon charcoal by the blowpipe flame, afterwards moistened with a few drops of *protonitrate of cobalt*, and again strongly heated, the mass assumes a BLUE COLOUR on cooling. This can only be used as a confirmatory test, as other substances, phosphates and readily fusible salts, exhibit the same reaction.

235. OXIDE OR SESQUIOXIDE OF CHROMIUM.—The colour of this oxide is green; its hydrate is bluish-gray. The salts of this oxide have a green or a violet colour; their solutions possess a beautiful green colour by reflected, and reddish-violet by transmitted light. The salts of this oxide, which are soluble in water, redden litmus paper. Sulphide of chromium is decomposed in contact with water into oxide of chromium and hydrosulphuric acid. The principal mineral from which this oxide is extracted is the CHROME IRON (FeO, Cr_2O_3), which is found principally in Sweden, in the Uralian Mountains, and in America.

236. When oxide of chromium, or any of its compounds, are fused with nitrate of soda or potash, and carbonate of soda, it becomes converted into a higher oxide, viz., CHROMIC ACID, which, combining with the soda, forms yellow chromate of soda. This soda salt must be dissolved in water and tested for chromic acid by adding acetic acid in excess, and then acetate of lead, when yellow chromate of lead* will precipitate. This test distinguishes it at once from all other substances.

237. If we add to a solution of sesquioxide of chromium in caustic soda or potash peroxide of lead in excess, and then boil the mixture for some time, the sesquioxide of chromium becomes converted into chromic acid by its reducing some of the per-

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* If the nitrate or carbonate of soda employed contain a trace of sulphate, there will be produced on the addition of acetate of lead, a *white* precipitate of sulphate of lead.

oxide of lead to the state of protoxide, and with this new-formed oxide the chromic acid unites, forming chromate of lead, which is soluble in the alkaline solution. If the liquid is filtered, the filtrate will be *yellow* from the dissolved chromate of lead, and if acetic acid be added in excess to the solution, chromate of lead, being insoluble in the acid, will precipitate.

238. *Borax* dissolves oxides of chromium and its salts, both in the inner and outer blowpipe flame; the bead, on cooling, assumes an EMERALD GREEN COLOUR. *Microcosmic salt* has the same effect.

239. In the fixed alkalies, a small quantity of oxide of chromium in the presence of a large quantity of peroxide of iron is totally insoluble; but a small quantity of the latter dissolves readily when a large quantity of the former is present. Under these circumstances, the two oxides are best separated from each other by fusing the mixed substances with *nitre* and *carbonate of soda,* and treating the fused mass with water; the CHROMATE OF POTASH dissolves in the liquid, whilst the PEROXIDE OF IRON remains behind.

240. PROTOXIDE OR OXIDE OF IRON.—The colour of this oxide is black; its hydrate is white, which, in the moist state absorbs oxygen from the air very rapidly, acquiring a grayish-green, and finally a brownish-red, colour. The salts of this oxide are white in their anhydrous, and green in their hydrated state; their solutions appear coloured only when very concentrated. They turn blue litmus paper red, and are decomposed at a red heat. When dissolved, they absorb oxygen from the air, the oxide being thereby converted into peroxide, which, in a neutral solution, is deposited as a yellow basic salt. Oxidizing agents, such as chlorine and nitric acid, effect this conversion more speedily.

241. *Ferrocyanide of potassium* (Cy_3 Fe, 2 K=Cfy, 2 K) produces, in solutions of protoxide of iron, a white precipitate of FERROCYANIDE OF IRON AND POTASSIUM (2 Cfy, K, 3 Fe), which speedily becomes *blue* by absorbing oxygen from the air. Free alkalies prevent the formation of this precipitate. It is insoluble in the dilute acids.

242. *Ferricyanide of potassium* ($Cy_6 Fe_2 3 K = Cfdy, 3 K$) produces a beautiful blue-coloured precipitate of FERRICYANIDE OF IRON (Cfdy, 3 Fe), which is insoluble in hydrochloric acid, but is decomposed with precipitation of oxide of iron by the alkalies. In highly dilute solutions of protoxide of iron, ferricyanide of potassium produces only a bluish-green coloration. If the solution is alkaline, it must be acidified with acetic acid; if it is acid, and the acidity is caused by one of the mineral acids, an alkaline acetate must be added, in sufficient quantity so that the base of the acetate may neutralize the free mineral acid (see 246).

243. PEROXIDE OR SESQUIOXIDE OF IRON.—This oxide which is abundantly spread through nature, has received from mineralogists the name of HÆMATITE. It is of a brownish-red colour, and is well known as rust of iron. Its salts usually possess a reddish-yellow colour. The soluble neutral salts of mineral acids redden litmus paper, and are decomposed by heat.

244. *Ferrocyanide of potassium* throws down, even from highly dilute solutions, a beautiful blue precipitate of FERROCYANIDE OF IRON (Prussian blue, $Cfy_3 Fe_4$), which is insoluble in acids, but is decomposed by the alkalies. In highly dilute solutions of this oxide of iron, only a blue tinge is produced at first; after long standing a scanty precipitate is formed. The same precautions are required in this case as in testing for protoxide with the ferricyanide.

245. *Ferricyanide of potassium* deepens the colour of the solution of persalts of iron to a ruddy brown, but causes no precipitate; if the ferricyanide contains a trace of ferrocyanide,* it will impart to the iron solution a greenish tinge.

246. The ferro- and ferri- cyanide of potassium are decomposed by the mineral acids, green-coloured solutions being formed. In testing, therefore, for iron in acid solutions, it is

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* The solution of ferricyanide of potassium ought to be made as it is wanted, as the ferricyanide decomposes when in a state of solution, a trace of ferrocyanide being formed.

necessary to avoid this error by the previous addition of an alkaline acetate.

247. Sulphocyanide of potassium (K, CyS_2)produces in neutral, and even in moderately acid, solutions of sesquioxide of iron a very intense blood-red, arising from the formation of a soluble SULPHOCYANIDE OF IRON. The colour disappears on the addition of an alkaline acetate, but is restored by adding to the solution dilute hydrochloric acid; it also disappears on the addition of alkalies, or of a large quantity of strong acid. This is by far the most delicate test for sesquioxide of iron.

The following SALTS, *being insoluble in Neutral and Alkaline Solutions, are precipitated along with the members of the Fourth Group.*[*]

PHOSPHATE OF ALUMINA, PHOSPHATE OF CHROMIUM, THE PHOSPHATES OF IRON, AND THE PHOSPHATES AND OXALATES OF THE ALKALINE EARTHS, WITH THE EXCEPTION OF OXALATE OF MAGNESIA.

248. PHOSPHATE OF ALUMINA behaves in the same way with reagents as pure alumina, with this exception, that it is insoluble in *acetic acid*, whilst pure alumina is soluble. The presence of phosphoric acid, when combined with alumina, may be detected by the following method:—After having *dissolved* the alumina compound in a small quantity of hydrochloric acid, *tartaric acid* must be added and then *ammonia* in *excess*. If on the addition of *sulphate of magnesia* to this solution a precipitate be formed, PHOSPHORIC ACID is present. When the quantity of acid present is small, the precipitate will not appear until after the lapse of some time; in all cases the formation of the precipitate is much promoted by agitation (see par. 491).

249. The phosphoric acid in phosphate of alumina may also be detected in the following way:—"Add carbonate of soda to

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[*] The student will do well to omit this section of the group until he has had some practice in detecting the more simple combinations of acid and base.

the hydrochloric acid solution until the free acid is nearly neutralized; mix with carbonate of baryta in excess, add solution of soda or potash, and boil. This process gives the alumina in solution, the phosphoric acid in a precipitate of phosphate of baryta. Dissolve this precipitate in hydrochloric acid, decompose by sulphuric acid, filter, and test the filtrate with sulphate of magnesia, with addition of chloride of ammonium and ammonia."—*Fresenius.*

250. Phosphoric acid may be detected in almost all salts and most minerals containing it, in the following way:—"If some molybdate of ammonia is mixed in a test-tube with hydrychloric acid or nitric acid in sufficient quantity to redissolve the precipitate which forms at first, and a little of a very dilute fluid containing phosphoric acid is then added, and the mixture gently warmed, the fluid acquires an intensely yellow colour, and after some time a yellow precipitate separates, which is insoluble in hydrochloric acid. As the yellow compound is decomposed by free phosphoric acid, an excess of the fluid containing the phosphoric acid must be carefully avoided. The yellow precipitate may, when it has subsided, be perceived even in dark-coloured fluids."—*Fresenius.*

251. PHOSPHATE OF THE SESQUIOXIDE OF CHROMIUM behaves in the same way with reagents as the sesquioxide, with this exception, that it is insoluble in *acetic acid*, in which reagent the latter is soluble. The presence of phosphoric acid, when combined with sesquioxide of chromium, may be detected in the same way as when this acid is combined with alumina. To ascertain whether sesquioxide of chromium and the phosphate of the sesquioxide of chromium are both present in the precipitate produced by boiling the fixed alkaline solution, dissolve the precipitate produced on boiling in hydrochloric acid, add an *alkaline acetate* in excess; if a precipitate is produced, the PHOSPHATE is present, filter off, and to the filtrate add *ammonia* in excess; if a precipitate is produced the OXIDE is present.

252. PHOSPHATE OF IRON behaves in the same way with reagents as the peroxide, with this exception, that it is insolu-

ble in *acetic acid*, in which reagent the latter is soluble. *Sulphide of ammonium* decomposes PHOSPHATE OF IRON,[*] precipitating the metal in the state of sulphide whilst the acid remains in solution in combination with the ammonia. The phosphoric acid is therefore sought for in the filtrate and not in the precipitate, when sulphide of ammonium has been employed as the precipitating reagent. The same method may be employed for the detection of phosphoric acid when combined with iron, as is employed when this acid is in combination with alumina.

253. PHOSPHATE OF LIME (bone earth $3CaO, PO_5$) is soluble in *acetic acid*. This salt may be decomposed in several ways. The following are those which are most applicable in qualitative analysis :—1. Dissolve the phosphate in a small quantity of hydrochloric acid; add to the solution *acetate of potash*, and after that a few drops of *perchloride of iron* (*consult* paragraph 487). PHOSPHATE OF IRON will be precipitated, whilst the LIME will remain in solution along with the excess of the perchloride of iron employed. To detect the LIME, throw down the iron by sulphide of ammonium, and add to the filtrate *oxalic acid*. If a precipitate be produced, lime is present. 2. Dissolve the phosphate in a small quantity of *nitric acid;* add to this solution *sub-nitrate of mercury*, and then *ammonia* slightly in excess; PHOSPHATE OF MERCURY along with the excess of OXIDE OF MERCURY will be precipitated, whilst the LIME will remain in solution, from which solution it will be thrown down on the addition of *oxalic acid*. Boil the mixed precipitate of phosphate of mercury and oxide of mercury in sulphide of ammonium; filter, and to the filtrate add *chloride of ammonium* and *sulphate of magnesia*; if a precipitate be produced, it proves the presence of phosphoric acid. The above remarks upon PHOSPHATE OF LIME apply to the corresponding salts of BARYTA, STRONTIA, and MAGNESIA.

254. OXALATE OF LIME is insoluble in *acetic acid*. By ignition, this salt, like all the other oxalates, is decomposed, a carbon-

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[*] The phosphates of alumina and chromium are not decomposed by sulphide of ammonium, they are precipitated unchanged by that reagent.

ate being left. To separate the oxalic acid from the lime, add to a *nitric acid solution* of this salt *subnitrate of mercury*. OXALATE OF MERCURY will be precipitated, whilst the lime, in the state of nitrate, will remain in solution along with the excess of subnitrate of mercury employed. To detect LIME, precipitate the mercury by ammonia, and add to the filtrate *oxalic acid*. OXALATE OF MERCURY is decomposed by boiling it in *sulphide of ammonium*, the metal being precipitated as sulphide, whilst the acid remains in combination with ammonia, in which solution it may be detected on the addition of any soluble *lime salt*. The above remarks apply to the corresponding SALTS OF BARYTA and STRONTIA.

255. *The following precautions are to be attended to in the analysis of this section:*—Before dissolving the precipitate produced by ammonia, it must be completely freed by washing from all trace of that reagent. Frequently a small precipitate will appear after boiling the caustic soda solution, when oxide of chromium is absent; the presence of this member must therefore in all cases be confirmed by other tests. Alumina and phosphate of alumina are sometimes overlooked by the operator, from his neglecting to add acetic acid in excess. The precipitate produced by caustic soda, after being well washed, should be dissolved in as small a quantity of nitric acid as possible, to which solution a moderate quantity of tartaric acid should be afterwards added, and finally ammonia in excess; the solution ought, after the addition of these reagents, to be well agitated, and time allowed for the separation of the precipitate. In testing for phosphoric acid in the ammoniacal solution, a precipitate will frequently be formed on the addition of sulphate of magnesia when phosphoric acid is absent. To distinguish the phosphate precipitate from this, the precipitate produced ought to be dissolved in tartaric acid, and ammonia added in excess. If a precipitate again appears, after agitating the liquid and allowing it to stand, it must be due to the presence of phosphoric acid. The precipitate produced by ammonia in the tartaric acid solution must be well washed before dissolving it in dilute nitric acid. A slight turbidness will

TABLE V.—PRECIPITATE PRODUCED BY AMMONIA IN THE HYDROSULPHURIC ACID FILTRATE.

Dissolve in boiling dilute Nitric Acid.—Add an excess of Caustic Soda in the cold.

<table>
<tr>
<td colspan="3">FILTRATE
SESQUIOXIDE of CHROMIUM; PHOSPHATE of CHROMIUM; ALUMINA; PHOSPHATE of ALUMINA.
<i>Boil for some time.</i></td>
<td colspan="5">PRECIPITATE
PEROXIDE of IRON, PERPHOSPHATE of IRON, AND WHEN IN COMBINATION WITH OXALIC OR PHOSPHORIC ACIDS, BARYTA, STRONTIA, LIME; ALSO MAGNESIA, WHEN IN COMBINATION WITH PHOSPHORIC ACID.
<i>Dissolve in boiling dilute Nitric Acid, then add Tartaric Acid, and finally Ammonia in excess.</i></td>
</tr>
<tr>
<td colspan="2">FILTRATE
ALUMINA; PHOSPHATE of ALUMINA.
<i>Add Acetic Acid in excess.</i></td>
<td rowspan="5">PRECIPITATE of CHROMIUM.
Examine for the Phosphate and Oxide in way stated in par. 251.</td>
<td colspan="2">FILTRATE
PERNITRATE of IRON; PERPHOSPHATE of IRON.
<i>Divide the solution into two parts.</i></td>
<td colspan="3">PRECIPITATE
The PHOSPHATES and OXALATES of the ALKALINE EARTHS.
<i>Dissolve in Nitric Acid, and add Subnitrate of Mercury.</i></td>
</tr>
<tr>
<td>FILTRATE
ALUMINA; <i>add Phosphate of Soda.</i></td>
<td rowspan="4">PRECIPITATE
PHOSPHATE of ALUMINA.</td>
<td><i>To one part add Acetic Acid, until the solution possesses an acid reaction; then add Ferrocyanide of Potassium.</i></td>
<td><i>If iron has been found, add to the other part Chloride of Ammonium and Sulphate of Magnesia.</i></td>
<td colspan="2">FILTRATE
BARYTA, STONTIA, or LIME, <i>originally in combination with</i> OXALIC ACID <i>and the</i> PHOSPHATES <i>of the</i> ALKALINE EARTHS, <i>along with the excess of Subnitrate of Mercury.</i>
<i>Add Ammonia slightly in excess.</i></td>
<td rowspan="2">PRECIPITATE
OXALATE of MERCURY.
<i>Confirm the presence of</i> OXALIC ACID, <i>by boiling the Mercury precipitate in Sulphide of Ammonium;</i> filter, and acidify with acetic acid; filter if necessary, and then add to the solution <i>Sulphate of Lime.</i></td>
</tr>
<tr>
<td rowspan="3">PRECIPITATE.
PHOSPHATE of ALUMINA.</td>
<td><i>If a blue precipitate is formed, it shows the presence of</i> IRON.</td>
<td><i>If a precipitate is formed after agitating the fluid and allowing it to stand for some time, it shows the presence of</i> PHOSPHORIC ACID.</td>
<td rowspan="3"><i>Filtrate</i>
BARYTA, STRONTIA, LIME, and MAGNESIA.
<i>Examine the filtrate for the Alkaline Earths, in the usual way.</i></td>
<td><i>Precipitate</i> •
PHOSPHATE OF MERCURY along with the excess of Oxide of Mercury. <i>Boil the precipitate in Sulphide of Ammonium; filter, and to the filtrate add Chloride of Ammonium and Sulphate of Magnesia.</i></td>
</tr>
<tr>
<td colspan="2">NOTE.—To ascertain whether there was any <i>Iron,</i> uncombined with Phosphoric Acid, <i>add to the original solution Acetate of Soda; filter, and to the filtrate add Ferrocyanide of Potassium.</i></td>
<td rowspan="2"><i>If a Precipitate is formed after agitating the liquid and allowing it to stand for some time, it proves the presence of</i> PHOSPHORIC ACID.</td>
<td rowspan="2"><i>If a precipitate is formed,</i> OXALIC ACID <i>is present.</i></td>
</tr>
<tr>
<td colspan="2">If a blue precipitate is formed, it proves that all the iron did not exist as phosphate.</td>
</tr>
</table>

generally be formed on the addition of nitrate of mercury to the nitric acid solution, even in the absence of oxalic acid, owing to the nitric acid containing a slight trace of chlorine.

256. The following is another method for the separation of the members of the fourth group and the phosphates and oxalates which are precipitated along with them by the group reagent; the precipitate produced by ammonia, after being well washed, is ignited upon a piece of platinum foil, or in a small crucible; if one or more of the three oxalates (baryta, strontia, and lime) are present, they will be converted by the ignition into *carbonates;* dissolve the ignited precipitate in as small a quantity of boiling dilute hydrochloric acid as possible; if it dissolves with *effervescence*, one or more of the three oxalates are present; examine the solution in this case according to par. 257. If the solution is unattended with effervescence, the three oxalates are absent; examine the solution in this case according to par. 258.

257. When the solution is attended with effervescence add *ammonia* in excess to the solution, warm, and filter; the filtrate will contain the base or bases originally combined with oxalic acid; examine for these bases in the way directed in the second group, par. 165; wash the precipitate very well, then dissolve it in as small a quantity of boiling dilute hydrochloric acid as possible; examine the solution according to par. 258.

258. Add one of the fixed alkalies in excess in the *cold* to the hydrochloric acid solution; if PHOSPHATE OF IRON, or PEROXIDE OF IRON, or any of the PHOSPHATES OF THE ALKALINE EARTHS are present, they will be *precipitated;* whilst ALUMINA and SESQUIOXIDE OF CHROMIUM and their PHOSPHATES will be retained in *solution;* examine the precipitate according to par. 260, and the solution according to par. 259.

259. *Boil* the fixed alkaline solution for some time; if a precipitate is produced, it is due to the presence of SESQUIOXIDE OF CHROMIUM, or its phosphate; filter when a precipistate is produced, add to the filtrate, or to the solution, with

out filtering, when no precipitate has been produced,* *acetic acid* in excess, PHOSPHATE OF ALUMINA, if present, will be precipitated; add to the filtrate *ammonia* in excess, when ALUMINA if present, will be precipitated. Dissolve the chromium precipitate in as small a quantity of boiling dilute hydrochloric acid as possible, add an *alkaline acetate* in excess, PHOSPHATE OF CHROMIUM, if present, will be precipitated; to the filtrate add *ammonia* in excess; if SESQUIOXIDE OF CHROMIUM be present, it will be precipitated by the ammonia.

260. After the precipitate produced by the fixed alkali has been well washed, it must be dissolved in as small a quantity of boiling dilute hydrochloric acid as possible, then add one of the *alkaline acetates* in excess, and *boil* for some minutes; the PHOSPHATE OF IRON and the OXIDE (the latter as basic peracetate), will be *precipitated*, if present, whilst the PHOSPHATES OF THE ALKALINE EARTHS will remain in *solution;* examine the solution according to par. 261, and examine the precipitate for phosphoric acid in the following way:—Digest the precipitate in *sulphide of ammonium* for a few minutes, then filter and examine the filtrate for PHOSPHORIC ACID, according to par. 484. To ascertain whether there was any iron uncombined with phosphoric acid, add to the original solution an *alkaline acetate;* filter, and to the filtrate add *ferrocyanide of potassium.* If a blue precipitate is formed, it proves that all the IRON *did not* exist as phosphate.

261. To the solution add *sesquichloride of iron*, drop by drop; if no precipitate is produced on the addition of the first two drops, the PHOSPHATES OF THE ALKALINE EARTHS *are absent;* if a precipitate is produced, continue the addition of the perchloride of iron until the solution is of a slightly reddish colour, then boil until the excess of iron is removed from the solution by boiling, then filter, and examine the filtrate for BARYTA, STRONTIA, LIME, and MAGNESIA in the usual way.

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* If no precipitate is produced on boiling the fixed alkaline solution, a portion of the precipitate produced by the group reagent ought to be examined for chromium, in the way directed at par. 228.

262. When substances are examined, the nature of which is a sufficient proof that the oxide of chromium and its phosphate, and the phosphates of baryta and strontia, and the oxalates of baryta, strontia and lime must be absent, as in the case of soils, natural and artificial manures, &c.;* the last method may be much simplified;—the precipitate produced by the group reagent, need not be ignited, the free alkali need not be added in the cold, and after its addition the mixture may be boiled, in order to hasten the filtration; and lastly, lime and magnesia are the only alkaline earths which have to be sought for.

263. When substances are examined, the nature of which is a sufficient proof that oxalate of lime is the only oxalate, and that phosphate of lime and phosphate of magnesia are the only phosphates of the alkaline earths which can be present, as in the case of *guano*, *urine*, *urinary deposits*, &c., † a simpler method may be employed for detecting and separating these salts than the one given in Table V: after having separated them from all the other substances in the way directed in Table V, dissolve the precipitate produced by ammonia in the tartaric acid solution in a small quantity of hydrochloric acid and to the solution add *acetate of soda* in excess. OXALATE OF LIME, if present, will be precipitated, whilst the phosphates of lime and magnesia will remain in solution. Filter, and to the filtrate add *oxalic acid*, which will precipitate the LIME existing originally as PHOSPHATE in the state of OXALATE. PHOSPHATE OF MAGNESIA will be precipitated from this filtrate on the addition of ammonia in excess.

264. The BORATES and FLUORIDES of BARYTA, STRONTIA, and LIME, are also precipitated by *ammonia;* but they are not completely precipitated by ammonia in the presence of chloride of ammonium; therefore, a portion at least of the bases of these salts will be found as a member of the second group,

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* Guano generally contains oxalate of lime, examine the ammonia precipitate of this manure according to par. 263.

† Of course in such substances as guano, urine, and urinary deposits, oxide of chromium and its phosphate cannot be present.

and the acids in these salts will be discovered in the ordinary examination of the acids, for these reasons we have not included these salts in the group; but it is necessary for the student to know that, when present in considerable quantities, they are in part precipitated by ammonia, as otherwise their precipitation by ammonia might occasion him much perplexity.

APPENDIX TO THE FOURTH GROUP.

265. SESQUIOXIDE OF URANIUM ($U_2 O_3$). This oxide is of a brick-red colour, its hydrate is yellow; by ignition it loses part of its oxygen, being converted into $U_3 O_4$, the colour of which is a very dark green, approaching black. The sesquioxide dissolves in acids, forming salts, the solutions of which have a fine yellow colour, and redden blue litmus paper. Hydrosulphuric acid reduces this oxide to the state of protoxide, which attracts oxygen from the air, becoming converted into the sesquioxide again: oxidizing agents have the same effect.

266. *Sulphide of ammonium precipitates*, from alkaline solutions of this oxide a brownish coloured precipitate, which subsides slowly, and is readily soluble in acids, even in acetic acid; chloride of ammonium promotes the formation of the precipitate.

267. The *volatile* and *fixed alkalies* precipitate this oxide from its solutions completely, in the form of a yellow precipitate, which is insoluble in an excess of the reagent.

268. *Carbonate of ammonia* produces a yellow precipitate, which is soluble in an excess of the reagent, but is deposited again from this solution on boiling. It differs from sesquioxide of iron in its behaviour with this reagent, which it so closely resembles in its behaviour with the other reagents. Bicarbonate of potash or soda produces a yellow precipitate which dissolves readily in an excess of the reagent.

269. *Ferrocyanide of potassium* produces in solution of this

oxide a fine brown-red precipitate; this is a very delicate test for uranium.

270. TITANIC ACID ($Ti\ O_2$)—This acid, although comparatively a rare substance, occurs in some iron ores, and as it is considered by some to improve the quality of the iron, we have given, on this account, a short description of its properties, and the mode of detecting it.

271. The anhydrous acid varies in colour, according to the mode of its preparation; it sometimes appears as a white powder, which, when heated, acquires during the time it is heated, a yellow tint, and sometimes it appears in the form of small lumps of a reddish-brown colour. The hydrated acid (TiO_2, HO) is white. The anhydrous acid is insoluble in water and acids, with the exception of concentrated sulphuric acid, which dissolves it with the aid of heat; when fused with bisulphate of soda, the fused mass dissolves completely in a large quantity of cold water; when fused with carbonate of soda it combines with the soda, forming bititanate of soda, which, on the addition of water, is decomposed into soda, which dissolves in the water, and titanate of soda, which is insoluble in that liquid, but which is soluble in hydrochloric acid.

272. The hydrated acid in the moist state, and also when dried at a temperature not exceeding 212° F., is soluble in dilute acids, especially hydrochloric and sulphuric. When the acid solutions of titanic acid are greatly diluted with water, and boiled for a long time, the titanic acid is completely precipitated as a white powder, insoluble in dilute acids; this precipitate possesses the marked property of passing through the filter when washed, unless an acid or chloride of ammonium is added along with it. It is precipitated from its acid solutions* in the form of a milky-white precipitate by the volatile and fixed alkalies and their carbonates, by carbonate of baryta, and by sulphide of ammonium;

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* Not in the presence of tartaric acid, or other non-volatile organic matter.

the precipitate is insoluble in an excess of the precipitant; but if it has been precipitated by any of these reagents in the cold, and washed with cold water, it is soluble in dilute hydrochloric or sulphuric acid.

273. When the solution of titanic acid in hydrochloric acid does not contain too much free hydrochloric acid—when, for example, it has been prepared in such a way that part of the titanates treated by the hydrochloric acid has remained undissolved, and has been filtered from the solution diluted with water—the solution of the acid behaves with the reagents named in *a*, *b*, and *c*, in the way described in these paragraphs.

(*a*) *Infusion of galls* produces in the solution a reddish orange-yellow precipitate of TANNATE OF TITANIC ACID.

(*b*) *Ferrocyanide of potassium* gives a dense orange-brown precipitate; the precipitate is soluble in an excess of the precipitant.

(*c*) White precipitates are produced by adding to the solution *dilute sulphuric*, *arsenic*, *phosphoric*, or *tartaric acid*, but more especially *oxalic acid;* these precipitates are completely redissolved in an excess of the precipitating acid, and likewise by hydrochloric acid; the precipitate produced by oxalic acid is the most insoluble.

274. If a strip of ZINC, IRON, or TIN be introduced into a solution of titanic acid in hydrochloric acid, the solution will become blue; and from this, a reddish or violet precipitate will separate, which gradually oxidizes into the white titanic acid.

275. Pure titanic acid where fused with *microcosmic salt* in the inner blowpipe flame, gives, after continued exposure, a bead which assumes a violet colour on cooling; this reaction, which is rendered easier on addition of metallic tin, disappears in the outer flame. If iron be present, a yellow or blood-red bead will be produced in the reducing flame.

276. Titanic acid, from its great similarity to silicic acid, is frequently overlooked in the analyses of silicates, although it occurs in many instances in some quantity. When metallic

zinc is fused in conjunction with minute quantities of titanic acid, after the combustion of the zinc and clearing of the bead on cooling, a very distinct coloration is always produced, whereas, the button of microcosmic salt and titanic acid gives no reaction in the ordinary way. By this test, titanic acid may be found in pig-iron, and in most cases, when any residue is left by treating silica with hydrofluoric acid (*Riley*).

FIFTH GROUP.

PROTOXIDE OF TIN. PEROXIDE OF TIN. OXIDE OF ANTIMONY. ARSENIOUS ACID. ARSENIC ACID. PEROXIDE OF GOLD. PEROXIDE OF PLATINUM.

277. All the members of this group possess, in a greater or less degree, the character of acids. Arsenious and arsenic acids are soluble in water; the rest are insoluble, not only in water, but likewise in nitric acid. They are all readily soluble in concentrated hydrochloric acid. In the state of sulphides they behave with different reagents in the following manner:—The protosulphide and bisulphide of tin, with the sulphide of antimony, are insoluble in nitric acid, but dissolve readily in concentrated hydrochloric acid; whereas sulpharsenious and sulpharsenic acids are insoluble in hydrochloric acid, but are easily soluble in concentrated nitric acid. These different sulphides are readily dissolved by the alkalies and alkaline sulphides, from which solutions they are again precipitated unaltered on the addition of any acid in excess. The sulphides of gold and platinum are insoluble both in hydrochloric and nitric acid, but are easily soluble in aqua regia (a mixture of the two acids). They also dissolve with difficulty in the alkalies and alkaline sulphides.

278. As gold and platinum are seldom met with in ordinary analyses, and as many of their properties render them perfectly

distinct from the rest of the members, it has been found of advantage to subdivide the group. The first division comprises the OXIDES of TIN, ANTIMONY, and ARSENIC; the second, the OXIDES of GOLD and PLATINUM.

FIRST DIVISION.

279. The precipitate produced by the general reagent, after having been well washed, must be treated with a dilute solution of *carbonate of ammonia.* Both SULPHIDES of ARSENIC, being soluble in that reagent, will pass into solution; whilst the SULPHIDES of ANTIMONY and TIN, being insoluble, will remain undissolved. The solution must be separated from the insoluble sulphides by filtration. If a *yellow precipitate* be produced on the addition of *hydrochloric acid* to the filtrate, one or both SULPHIDES of ARSENIC must be present. The substance which was insoluble in carbonate of ammonia, after having been well dried, must be mixed with three parts of *nitrate of ammonia,** and the mixture projected in small portions into a porcelain crucible containing two parts of nitrate of ammonia in a state of liquefaction. After all fuming has ceased, the residue should be gently ignited for a short time and then allowed to cool. The residue must be subsequently heated with a saturated solution of *tartaric acid.* If complete solution takes place, OXIDE of ANTIMONY only can be present. If a portion remain undissolved by the tartaric acid, it indicates the probable presence of TIN. When complete solution does not take place, the liquid must be filtered, and to the filtrate must be added *hydrochloric acid,* and subsequently *hydrosulphuric acid.* If an *orange-red-coloured precipitate* be formed, OXIDE of ANTIMONY is present. The substance insoluble in tartaric acid must be examined for tin by fusing it

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* When the amount of precipitate is so small that little or nothing can be detached from the filter, the precipitate as well as the filter, after having been cut into small pieces, must be mixed up with the nitrate of ammonia, and subsequently projected into the crucible.

with *carbonate of soda* and *cyanide of potassium*, as directed under the special remarks of the peroxide of that metal.

280. *The following precautions must be attended to in analysing this group*:—The mixed precipitate must be agitated in a test-tube for a few seconds only, with a dilute solution of carbonate of ammonia,* and then quickly filtered. When only a slight trace of arsenic is present, the carbonate of ammonia solution, on the addition of hydrochloric acid, will simply assume a slight yellow colour, no distinct precipitate being formed. When arsenic is present, the original solution must be examined to ascertain in what state it exists, whether as arsenious or arsenic acid.

281. Antimony and arsenic may also be separated from tin and from each other in the following manner:—The sulphides, precipitated from their solutions in alkalies or alkaline sulphides, are dissolved in nitro-hydrochloric acid, and the solution, thus obtained, poured into a hydrogen-apparatus so arranged as to allow the gas to be washed with a dilute solution of acetate of lead† which absorbs any hydrochloric acid or sulphuretted hydrogen, and to pass the mixture of antimonide, arsenide, and free hydrogen, into a test-tube half filled with concentrated nitric acid, which converts the antimony and arsenic into antimonic, arsenious, and arsenic, acids; the gas ought to be passed through the acid moderately slow. The nitric acid solution obtained after the gaseous mixture has passed for about a quarter of an hour, is evaporated; and the residue is exposed to a tolerable heat upon the sand-bath, in order to expel the last traces of nitric acid, which is an essential condition of success, inasmuch as antimonic acid is slightly soluble in water containing nitric acid. The residue is now treated with warm water, which dissolves the arsenious and arsenic acids, but leaves undissolved the antimonic acid: to the solution is added nitrate of silver, and the solution is

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* The dilute solution must be prepared by dissolving one ounce of solid carbonate of ammonia in twelve fluid ounces of water.

† A tube containing glass-splinters, moistened with a solution of acetate of lead, may be employed in place of the wash-bottle.

then very cautiously neutralized with ammonia, when a mixture of arsenite and arseniate of silver precipitates. The antimonic acid, which did not dissolve in the water, is dissolved in as small a quantity of nitro-hydrochloric acid as possible, and the solution evaporated as far as possible, and then tested with sulphuretted hydrogen water, when, if any antimony is present, the liquid at once assumes an orange-yellow colour; and, on boiling, decidedly orange-yellow flakes are separated. In order to detect the tin, the metallic precipitate is washed off the zinc in the generating bottle, and boiled with hydrochloric acid, when chloride of tin is formed, which may be detected by the well-known reaction with chloride of mercury.

282. To effect the detection of small quantities of arsenic, in presence of a large quantity of antimony, the above process may be advantageously modified by passing the washed gases into a solution of nitrate of silver instead of into nitric acid; the whole of the antimony is precipitated as antimonide of silver, while every trace of arsenic remains in solution in the form of arsenious acid. On neutralising the liberated nitric acid by ammonia, the characteristic yellow arsenite of silver is precipitated. If the gas has been passed for a long time, the solution is sometimes free from silver. In this case, the precipitate of arsenite of silver appears only after the addition of a drop of nitrate of silver. The antimony may be most readily detected by heating the precipitate, thoroughly freed from arsenious acid by boiling water—with tartaric acid and water to boiling. This will dissolve the antimony alone, which may then be readily detected by means of hydrosulphuric acid in the solution acidified with hydrochloric acid (*A. W. Hoffmann*).

SPECIAL REMARKS.

283. Oxide of Tin (SnO).—This oxide is black, its hydrate being white. Nitric acid and nitrates in a state of fusion convert it into the peroxide, which is insoluble in an excess of the acid. The protosalts of tin are colourless, and are decomposed

by heat. The soluble neutral salts redden litmus paper, and are decomposed, in the presence of much water, into soluble acid and insoluble basic salts. The addition of water therefore to the protosalts of tin produces a milkiness which disappears on the addition of hydrochloric acid. Sulphide of tin (SnS) is of a dark brown colour.

284. The *alkalies* and their *carbonates* throw down from solutions of this oxide the HYDRATE (SnO, HO), which is easily soluble in solutions of the fixed alkalies, but insoluble in ammonia and the alkaline carbonates.

285. All protosalts of tin are powerful reducing agents, from the great affinity they have for an additional quantity of oxygen. Many metallic oxides, such as the oxides of gold, silver, and mercury, are reduced to the metallic state in their presence; whilst other oxides, such as peroxide of iron and oxide of copper, are reduced to a lower degree of oxidation.

286. *Perchloride of gold* produces in solutions of protosalts of tin, containing a small quantity of free nitric acid, a beautiful PURPLE PRECIPITATE (purple of Cassius).

287. If a solution of a PROTOSALT OF TIN is added to a mixture of *ferricyanide of potassium* and *sesquichloride of iron*, *Prussian blue* precipitates immediately, owing to the reduction of the ferricyanide. This delicate test for a protosalt of tin can only be conclusive in cases where there are no other reducing agents present.

288. Solution of protochloride of mercury produces in solutions of protoxide of tin a white precipitate of subchloride of mercury, owing to the protosalt of tin withdrawing half the chlorine from the protochloride of mercury. If sufficient quantity of the tin-compound be present, it removes, after a time, all the chlorine from the mercury; the colour of the precipitate then becomes gray. Since this reaction takes place even in highly dilute solutions, and in the presence of much free hydrochloric acid, it is very valuable for the detection of oxide of tin.

289. PEROXIDE OF TIN (SnO_2).—This oxide is of a light

straw colour: its hydrate is white. Nitric acids converts metallic tin and its protoxide into the hydrated peroxide which is deposited in the form of a white powder. A peroxide of tin is likewise precipitated from persalts of tin, on the addition of caustic soda to their solutions. These hydrates, although they have the same composition, are perfectly distinct in their chemical properties. The one formed by the action of nitric acid is insoluble, both in acids and the fixed alkalies; the other is soluble in these reagents. These modifications are capable of being transformed into each other. The insoluble one is rendered soluble by fusion with the carbonated alkalies; the soluble is converted into the insoluble form by ignition. Bisulphide of tin (SnS_2) is of a yellow colour. The usual mineral of this metal is the peroxide (*tin stone* SnO_2).

290. The *alkalies* and their *carbonates* precipitate from solutions of persalts of tin the HYDRATE, which is soluble in the fixed caustic alkalies, but insoluble in ammonia and the alkaline carbonates.

291. If per- or proto-compounds of tin be mixed with equal parts of *carbonate of soda* and *cyanide of potassium*, and the mixed mass be subjected, upon a charcoal support, to the inner blowpipe flame, *ductile metallic grains of* TIN will be obtained, unaccompanied by any incrustation upon the charcoal.

292. OXIDE OF ANTIMONY (SbO_3).—This oxide occurs either in the form of white brilliant crystalline needles or as a grayish white powder, assuming the one or the other of these forms according to its mode of preparation. It fuses at a gentle red heat, and, when exposed to a higher temperature, volatilizes unaltered. The solubility of this oxide in tartaric acid distinguishes it from the other members of the group. When fused along with nitrates, it is converted into a higher oxide (antimonic acid, SbO_5).

293. Some of the salts of antimony are decomposed by ignition; some are volatilized unaltered. The soluble neutral salts redden litmus paper. When treated with a large amount of water, they are decomposed into soluble acid and insoluble basic salts. In this respect they resemble the salts of bismuth;

with this exception, that the insoluble basic salts of antimony dissolve in tartaric acid, whilst the corresponding salts of bismuth are insoluble. Sulphide of antimony (SbS_3) is of an orange-red colour. The principal mineral of this metal is the sulphide.

294. The *alkalies* and their *carbonates* throw down from solutions of antimony a bulky precipitate of OXIDE OF ANTIMONY, which is soluble in the fixed caustic alkalies and the alkaline carbonates, but insoluble in ammonia.

295. *Metallic zinc* precipitates from all solutions of salts of teroxide of antimony, if they contain no free nitric acid, *metallic antimony* as a black powder. But if the solution contains free nitric acid, teroxide of antimony precipitates together with the metal. If a few drops of a solution of antimony, containing some free hydrochloric acid, are poured into a platinum dish (the inside of a platinum crucible cover), and a small piece of zinc introduced, hydrogen is evolved, and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions. Cold hydrochloric acid fails to remove the stain, which, however, may be immediately removed by warm nitric acid. *(Fresenius.)*

296. If a solution of teroxide of antimony in one of the fixed alkalies is mixed with a solution of nitrate of silver, a deep-black precipitate of suboxide of silver forms with the grayish-brown precipitate of oxide of silver. Upon now adding ammonia in excess, the oxide is redissolved, whilst the suboxide is left undissolved *(H. Rose)*. This very delicate test enables one to detect readily the presence of teroxide of antimony in the presence of antimonic acid.

297. If a solution of teroxide of antimony is brought into contact with zinc and dilute sulphuric acid, the zinc oxidizes not only at the expense of the water, but also at the expense of the teroxide of antimony; the antimony is, consequently, reduced to the metallic state: a portion of the antimony, however, at the moment of its reduction, enters into combination with some of the liberated hydrogen, forming with that element a gaseous compound—terhydride of antimony (SbH_3).

"If this gaseous compound be dried by passing it through a tube, the anterior portion of which is loosely filled with cotton wool, and the remoter part with chloride of calcium, and be then allowed to escape from a tube of *hard glass* drawn out to a fine point, the presence of antimony may be recognised by the following reactions:

298. "1st. The gas will burn with a *bluish-green flame*, emitting white fumes of *teroxide of antimony*, which may be condensed in a cold beaker, dissolved in *hydrochloric acid* and tested with *hydrosulphuric acid.*

299. "2nd. If the inner surface of a porcelain capsule be depressed upon the flame, a *black spot* of metallic antimony will be deposited upon it, which is lustrous, only when in thin layers. This coating of metal may be dissolved in *aqua regia* and tested. (The operator should take care to prove, before commencing this experiment, that the flame of the hydrogen itself deposits no spot upon porcelain.)

300. "3rd. The glass tube from which the gas issues should be heated with a spirit lamp, in the centre; a *lustrous mirror of antimony* will be deposited on the inside of the tube, immediately around the flame of the lamp, whilst the bluish-green tint of the hydrogen flame in great measure disappears.

301. "These reactions should be compared with those of terhydride of arsenic under similar circumstances.

302. "If granulated zinc be boiled with a solution of antimony, to which a very large excess of *potash* has been added, the hydrogen which is evolved is free from terhydride of antimony."

303. If compounds of antimony, mixed with *carbonate of soda* and cyanide of potassium, be exposed, upon a charcoal support, to the reducing flame of the blowpipe, brittle grains of *metallic* antimony will be formed, accompanied with a *white* incrustation on the charcoal.

304. ARSENIOUS ACID (AsO_3).—There are two varieties of this acid, which are perfectly distinct in their physical characters and chemical properties. One, from its appearance

is termed the vitreous, and the other the milky variety; when heated, they volatilize in white inodorous fumes. "If the operation is conducted in a glass tube, a sublimate is obtained, consisting of small brilliant octahedrons and tetrahedrons." Both kinds are more easily soluble in hot than in cold water. This acid is exceedingly poisonous; and being altogether inodorous, almost destitute of taste, and readily obtainable, is frequently employed as a poison. The best antidote is the moist and well-washed hydrated sesquioxide of iron.

305. This acid unites with bases, forming a class of salts called arsenites, which are all insoluble in water, with the exception of the alkaline arsenites. Sulpharsenious acid (AsS_3) is yellow, and soluble not only in the alkalies and alkaline sulphides, but likewise in the alkaline carbonates.

306. *Nitrate of silver* produces in neutral solutions of the arsenites a yellow precipitate of ARSENITE OF SILVER ($2AgO, AsO_3$), soluble in nitric acid and ammonia.

307. If recently precipitated TERSULPHIDE OF ARSENIC is digested with *sulphurous acid* and *acid sulphite of potash*, the precipitate is dissolved; upon heating the solution to boiling, the fluid turns turbid, owing to the separation of sulphur, which, upon continued boiling, is for the greater part redissolved. The fluid contains, after the expulsion of the sulphurous acid, arsenite and hyposulphite of potash. Tersulphide of antimony and bisulphide of tin do not show this reaction. (*Bunsen.*)

308. *Sulphate of copper* produces in neutral solutions of the arsenites a yellowish-green precipitate of ARSENITE OF COPPER ($2CuO, AsO_3$).

309. If to a solution of arsenious acid, or an arsenite, *caustic potash* be added in excess, and a few drops only of a dilute solution of *sulphate of copper*, and the liquid subsequently boiled, a red precipitate of *suboxide of copper* (Cu_2O) will fall down, whilst the solution will contain ARSENIATE OF POTASH. This test is particularly applicable in distinguishing arsenious from arsenic acid. It cannot be employed with safety as a

direct means for detecting arsenious acid, as many organic substances possess the property of reducing protoxide of copper to the state of suboxide.

310. "If to arsenious acid, no matter whether in the solid form or in solution, some *acetic acid* is added, and then *potash* in slight excess, the mixture evaporated to dryness, and the residue heated to redness in a small tube—or if a trace of arsenious acid is introduced into a narrow test-tube, and there covered with a somewhat larger quantity of acetate of soda, and heat applied—part of the arsenious acid is reduced, but there forms at the same time ALKARSIN (oxide of cacodyl, C_4H_6AsO), which makes its presence immediately known by its equally characteristic and formidable odour, which somewhat resembles that of sharp onions. This changes speedily to the not less characteristic odour of chloride of cacodyl, if the ignited contents of the tube are heated with a few drops of protochloride of tin."—*Bunsen.*

311. If clean metallic copper is boiled in a solution containing arsenious acid, and acidified with hydrochloric acid, the copper becomes coated with a *steel gray film* of metallic arsenic; if the quantity of arsenious acid is considerable, the reduced arsenic will separate from the copper, when the liquid is boiled for a considerable time, in *large black scales.* As many other metallic oxides are reduced to their metallic state under the same circumstances, it is necessary to submit the crust to further examination. This test, which is called "Reinsch's test," is particularly useful for the detection of arsenic in organic liquids or solids. "The suspected liquid is simply to be acidulated with about one sixth of its bulk of hydrochloric acid, and boiled. The solid tissue must be cut up into very small pieces, and boiled for some time in a mixture of about one part of hydrochloric acid with six of water, until the whole is completely disintegrated; then strained through muslin, or filtered through a previously wetted filtering paper.

312. "Into either of the above boiling liquids, dip the end of a piece of clean polished copper wire; examine the wire from time to time, and as soon as its surface acquires a gray metallic

discoloration, remove it, and add in its stead, fragments of fine copper gauze, continuing the supply as long as the last added piece assumes any definite alteration in colour.

313. "Remove the pieces of copper gauze, wash them in water, and dry them between folds of filtering paper; the deposit will not rub off unless the amount of arsenic be very large. If the arsenic exist in but very small quantity, the colour of the precipitated metal is bluish; otherwise, of a dark iron-gray tint. Holding the piece of gauze in the fingers, warm it over a flame, coil it up into a small compass, and introduce it into a reduction-tube: now apply heat cautiously; the arsenic will volatilize, oxidize, and condense in the cold part, in the form of a white crystalline sublimate. Several pieces of coated gauze may be thus treated successively, until a sufficiently obvious sublimate of arsenious acid is procured; by examination with a lens, or with the low power of a microscope, the crystals will be seen to consist of highly iridescent octo- and tetra-hedra."

314. File off the piece of tube containing the sublimate, boil it for a minute or two in a little water; test the water after the boiling for arsenious acid, one portion with hydrochloric and hydrosulphuric acids, and another portion with nitrate of silver.

315. Arsenic, as well as antimony, combines with hydrogen in its *nascent* state, forming an inflammable gaseous compound, which burns with a bluish white flame, water and arsenious acid being formed; water and teroxide of antimony being formed when terhydride of antimony is burned. When free access of air is prevented, the hydrogen only is oxidized, metallic arsenic (or if it is terhydride of antimony, metallic antimony) being deposited in a finely divided state.

316. If, therefore, a solution of arsenious acid or an arsenite be brought into contact with zinc and dilute sulphuric acid, the zinc oxidizes not only at the expense of the water, but also at the expense of the arsenious acid; and the arsenic at the moment of its reduction, enters into combination with

the hydrogen, forming with that element the gaseous compound terhydride of arsenic (AsH_3): this gaseous compound was discovered by the late Mr. Marsh, and applied by him in the detection of arsenic. If the reduction of the arsenious acid, and the conversion of the arsenic into terhydride of arsenic, be conducted in a flask fitted with an evolution-tube, the gaseous compound can then be subjected to the following experiments:—The evolution-tube must consist of a drying-tube, into one end of which is fitted a narrow tube of *hard glass*. The drying-tube is placed nearest the flask, and it is half filled with cotton wool, and half with fragments of chloride of calcium; the end nearest the flask is filled with the wool. The hard glass tube should be from six to nine inches long, and drawn out at one end, so as to form a jet, where the gas may be burned. The gas may be examined in the following manner:

317. 1st. "Terhydride of arsenic burns with a *livid blue flame*, producing *arsenious acid*, which may be condensed in a cold beaker, dissolved in *hot water*, and tested (especially with *nitrate of silver* and with *hydrochloric* and *hydrosulphuric acids*).

318. 2d. "By depressing the inner surface of a porcelain capsule* upon the flame, a *black* (generally) *lustrous spot of metallic arsenic* is obtained (this experiment should always be tried with the hydrogen flame,† before the arsenical solution is poured into the evolution-bottle); this spot may be tested by dissolving in *concentrated nitric acid*, evaporating just to dryness upon a sand bath, adding *water*, and afterwards *nitrate of silver*, with, if necessary, a little *dilute ammonia*, when a brick-red precipitate of *arseniate of silver* will be obtained; an antimony spot, when treated in this way

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* "The porcelain should not be allowed to remain in the flame for more than a second or two, since the minute spots would be dispelled if the porcelain were to become very hot."

† "A great obstacle to the employment of Marsh's test is the difficulty of obtaining zinc and sulphuric acid perfectly free from arsenic, for which they should be very carefully tested previously to use."

generally gives a slight dirty-white precipitate with nitrate of silver.

319. "The incrustation of arsenic (whether on a porcelain surface or in a glass tube) may be dissolved by solution of *chloride of lime*, which does not affect the antimony incrustation; this test may serve, to some extent, to distinguish the two metals, but it is not adequate to the detection of traces of antimony in a mirror of arsenic."—*Abel and Bloxam.*

320. The properties and reactions just described enable us to distinguish pure arsenical stains and mirrors from antimonial stains and mirrors, but they do not enable us to detect arsenic with positive certainty in the presence of antimony. To obtain positive evidence, the following method ought to be employed:—The central part of the glass tube (which ought to be free from lead) through which the gas passes should be heated to redness; this effects the decomposition of the gaseous compound, the metal being deposited in a finely divided state. A feeble stream of dry hydrosulphuric acid gas must now be transmitted through the tube, the metallic mirror being heated from its outward to its inward extremity. If only arsenic be present, the yellow sulphide of that metal will be formed. If antimony only be present, the orange or black sulphide of antimony will be produced; but if both metals be present, the corresponding sulphides will be formed; and the sulphide of arsenic, being the more volatile of the two, will be the further removed from the flame. A stream of dry hydrochloric acid gas must now be passed through the tube without the application of heat; by this means the sulphide of antimony will be converted into volatile chloride, which will entirely disappear; whilst the sulphide of arsenic will remain unaltered, and may be distinguished from any sulphur which may have separated, by dissolving readily in ammonia.

321. "If arsenites, or arsenious acid, or tersulphide of arsenic, are fused together with a mixture of equal parts of dry *carbonate of soda* and *cyanide of potassium*, the whole of the arsenic is reduced to the metallic state, and, if an easily reducible base, the latter also; the eliminated oxygen con-

verts part of the cyanide of potassium into cyanate of potash (KO, CyO). In the reduction of tersulphide of arsenic, sulphocyanide of potassium (K, CyS_2) is formed. The operation is conducted as follows:—Introduce the perfectly dry arsenical compound into the bulb of a small bulb-tube, and cover it with six times the quantity of a perfectly dry mixture of carbonate of soda and cyanide of potassium. The whole quantity must not more than half fill the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. Apply the heat of a spirit-lamp to the bulb, and continued this for a while, as the arsenic frequently requires some time for its complete sublimation. The metallic mirrors are deposited on the cold part of the tube: they are of exceeding purity. They are obtained from all arsenites whose bases remain either altogether untouched, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by its application, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for the direct production of arsenic from tersulphide of arsenic, and is in this respect superior to all other methods hitherto suggested. The delicacy of the reaction may be very much heightened by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by *Dr. V. Babo* and myself has shown that the most accurate and satisfactory results are obtained in the following manner."—*Fresenius.*

322. The apparatus consists of a flask or two-necked bottle capable of holding about eight or twelve fluid ounces; this flask or bottle is fitted with a funnel-tube, and a bent tube which dips into another and smaller flask. In the first flask carbonic acid is slowly generated from pretty large fragments of marble (no powder) and dilute hydrochloric acid; it is conveyed by the conducting-tube into the smaller flask, which is partly filled with concentrated sulphuric acid, in order to dry the gas. The conducting-tube from the small flask is bent at

right angles, and connected, by means of a cork, with the reduction-tube; this latter tube is made out of a piece of hard glass tube (combustion-tube) somewhat more than three eighths of an inch in diameter, and drawn out at one extremity to a long point; the length of the body of the tube should be about four inches, that of the point at least two and a half inches.

323. A mixture of three parts of dry *carbonate of soda* and one part of *cyanide of potassium* is dried in the water bath; one part of arsenical sulphide, or the arsenite, which has been also dried in the water bath, is mixed with about twelve parts of the well-dried mixture of carbonate of soda and cyanide of potassium. The mixture, before it has time to get damp, is put upon a narrow slip of card-paper bent into the shape of a gutter; it is then introduced into the tube, and the latter is turned half round upon its axis; the mixture falls upon the glass, and the gutter must be withdrawn. The mixture should be in the middle of the tube, and it ought not to occupy more than an inch. The reduction-tube must now be fixed, by means of the cork, to the conducting-tube of the small flask, and a moderate stream of carbonic acid ought to be evolved, by pouring some hydrochloric acid into the large flask, by means of the funnel-tube. Heat the reduction-tube, in its whole length, very gently with a spirit-lamp, until the mixture is perfectly dry; when all the water is expelled, moderate the gas stream so that only one bubble shall pass through the sulphuric acid in the small bottle in a second; the gas stream may be moderated by pouring water into the large flask by means of the funnel-tube. When the gas stream is moderated, apply the flame of a spirit-lamp to the shoulder of the tube; and when this part of the tube is red hot, apply the flame of a second and larger spirit-lamp, commencing at the end of the reduction-tube nearest the conducting-tube of the small flask, and heating along up to the mixture; continue to apply the flame at the part where the mixture is, until all the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses in the narrow part of the tube, whilst an extremely

minute portion only escapes through the fine point, imparting to the surrounding air the peculiar odour of garlic. Advance the flame of the second spirit-lamp slowly and gradually up to the first, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven into the narrow part. When this end has been attained, close the fine point of the tube by fusion, and apply heat, proceeding from the closed point towards the part where the greater part of it is condensed; by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner, perfectly distinct mirrors of arsenic may be produced from as little as the one three-hundredth part of a grain of tersulphide of arsenic. No mirrors are obtained by this process from tersulphide of antimony, nor from any other compound of antimony.

324. If a solution containing arsenious acid, or an arsenite, be mixed with a large excess of a concentrated solution of caustic potash, and boiled with fragments of granulated zinc, terhydride of arsenic is evolved, and may be readily recognised by allowing it to pass on to a piece of filter-paper moistened with a solution of nitrate of silver; the paper assumes a purplish-black colour, even when a small quantity of arsenic is present. This test serves to distinguish arsenic from antimony (*Fleitmann*).

325. Arsenious acid, when mixed with a little carbonate of soda, and subjected to the inner blowpipe flame on charcoal, evolves a peculiar garlic odour, supposed to arise from a lower oxide. The vapours of arsenious acid, when sublimed from a piece of glass, possess no odour.

326. ARSENIC ACID (AsO_5).—This oxide is white; it is deliquescent and strongly acid, forming, with bases, a class of salts called arseniates, which are all insoluble in water, with the exception of the alkaline arseniates. It fuses at a low red heat without undergoing decomposition, but at a higher temperature is resolved into oxygen and arsenious acid, which volatilize. Sulphurous acid, aided by a gentle heat, reduces it

likewise to this lower state of oxidation. The metal arsenic is found in nature principally as sulphide.

327. *Nitrate of silver* produces, in neutral solutions of the arseniates, a reddish-brown precipitate of ARSENIATE OF SILVER ($3\ AgO,\ AsO_5$), soluble in dilute nitric acid and in ammonia.

328. *Sulphate of copper* produces, in neutral solutions of the arseniates, a greenish-blue precipitate of ARSENIATE OF COPPER ($2\ CuO,\ HO,\ AsO_5$).

329. *Sulphate of magnesia*, in the presence of chloride of ammonium and ammonia, produces, in solutions of the arseniates, a white precipitate of ARSENIATE OF AMMONIA AND MAGNESIA ($2\ MgO,\ NH_4O,\ AsO_5$), soluble in acids.

330. In those reactions which depend upon the reduction of the arsenic to the metallic state, arsenic resembles arsenious acid.

SECOND DIVISION.

331. Gold and platinum produce reactions so decisive—the former with chloride of tin, and the latter with chloride of ammonium—that their presence may invariably be detected in the presence of all the other metals. The original solution may therefore in all cases be examined for these substances.

332. PEROXIDE OF GOLD (AuO_3).—This oxide is of a deep-brown colour, its hydrate being somewhat lighter in colour. They both dissolve readily in hydrochloric acid, but are insoluble in dilute oxygen acids. Persulphide of gold (AuS_3) is black.

333. The salts of the protoxide of iron precipitate gold as a *bluish-black* precipitate, which acquires a metallic lustre when rubbed.

334. A solution of protochloride of tin and some bichloride produce, even in very dilute solutions of gold, a purple precipitate (purple of Cassius), " the tint of which varies according to the quantity of gold present. The precipitate is insoluble in *dilute acids;* the gold solution should be first mixed with

the bichloride of tin, and the protochloride then added drop by drop. When the quantity of gold is extremely minute, a ***pink tinge*** pervades the solution.

335. "A very delicate method of applying this test is as follows:—*Sesquichloride of iron* is added to protochloride of tin until a permanent yellow colour is produced; the solution is then considerably diluted; the gold solution, having likewise been much diluted, is poured into a beaker, which is placed on a sheet of white paper; a glass rod is dipped into the iron solution, and afterwards into the gold solution, when, if even a trace of the precious metal be present, a ***blue or purple streak*** will be observed in the track of the glass rod.

336. "This purple-of-Cassius test has the advantage of being applicable even in very acid solutions."—*Abel and Bloxam.*

337. PEROXIDE OF PLATINUM (PtO_2).—This oxide is of a deep-brown colour, its hydrate is reddish brown. Both the oxide and its hydrate dissolve readily in hydrochloric acid, but with difficulty in the oxygen acids. Persulphide of platinum (PtS_2) is of a blackish-brown colour.

338. *Chloride of potassium* or *ammonium* produces, in solutions of platinum, yellow crystalline precipitates of POTASSIO-CHLORIDE OF PLATINUM and AMMONIO-CHLORIDE OF PLATINUM. The presence of free hydrochloric acid promotes the formation of these precipitates. Dilute solutions should be evaporated along with the chloride of potassium or ammonium and the free hydrochloric acid on the water bath to dryness, and the residue digested in weak spirits of wine until the excess of the alkaline chloride employed is dissolved.

339. Solutions of protochloride of tin produce, in solutions of binoxide of platinum, which contain much free hydrochloric acid, a dark *brown-red colour;* in exceedingly dilute solutions the colour is *yellow,* and becomes darker on standing. This test is a very delicate one for platinum. The dark brown colour is owing to the reduction of binoxide or bichloride of platinum to protoxide or protochloride.

SIXTH GROUP.

Oxide of Silver. Suboxide of Mercury. Oxide of Lead. Protoxide of Mercury, Teroxide of Bismuth. Oxide of Copper. Oxide of Cadmium.

340. The oxides of this group are insoluble in water. They all combine with nitric acid, forming soluble salts; many of them likewise form, with hydrochloric and sulphuric acid, soluble chlorides and sulphates; but a few give, particularly with the former acid, insoluble salts. This character permits of a subdivision of the group, which is fully exhibited under the head of its general properties.

341. In the state of sulphides they are insoluble, not only in the alkalies and alkaline sulphides, but likewise in the dilute mineral acids. They are therefore thrown down, both from their neutral, acid, and alkaline solutions, by sulphuretted hydrogen. They are all decomposed and rendered soluble in boiling *dilute* nitric acid, with the exception of PROTOSULPHIDE OF MERCURY.

342. The metallic radicals of these oxides possess the following properties:—*Cadmium* decomposes water at a red heat, and at common temperatures in contact with strong acids. *Copper*, *lead* and *bismuth* absorb oxygen at a red heat; their oxides are therefore not decomposed by heat alone. They do not decompose water except at a very elevated temperature, and even then very feebly; neither do they decompose it in the presence of strong acids or bases. The affinity of *mercury* and *silver* for oxygen is very feeble, so much so that their oxides are decomposed by heat alone, at a more or less elevated temperature. These metals do not decompose water, under any circumstances; they have therefore no tendency to rust when exposed to the air.

343. This group may, as before noticed, be divided into two sections:

344. *a.* OXIDES which are precipitated by hydrochloric acid, viz., OXIDE OF SILVER, SUBOXIDE OF MERCURY, and OXIDE OF LEAD.

345. *b.* OXIDES which are not precipitated by hydrochloric acid, viz., PROTOXIDE OF MERCURY, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, and OXIDE OF COPPER.

346. The slight solubility of chloride of lead in water renders it impossible to confine this member exclusively to the first section—a portion of the chloride, varying according to the amount of liquid present, always remaining dissolved. This is finally precipitated along with the members of the second section on the addition of hydrosulphuric acid. If attention be paid to the following facts, they will frequently remove a source of much confusion:—1. If lead has been discovered in the first section, a precipitate must always be obtained on passing hydrosulphuric acid through the filtrate, even if no other member of the group be present. 2. If only a small quantity of lead be present, hydrochloric acid may cause no precipitate, as a sufficient quantity of water may be present to dissolve the chloride formed. In this case, all the lead will be found in testing for the members of the second section.

347. *First section.*—*Boiling water*, being poured upon the precipitate produced by hydrochloric acid, will remove the CHLORIDE OF LEAD, if present, which is ascertained by *sulphuric acid* producing in the filtrate a precipitate of SULPHATE OF LEAD. If a residue remain after removing the chloride of lead by adding successively to the mixed chlorides fresh quantities of boiling water, until the last washings give on the addition of sulphuric acid no further precipitate, it proves that either chloride of silver or subchloride of mercury (calomel), or both, must be present. *Ammonia* being added to this residue, dissolves the CHLORIDE OF SILVER, whilst the SUBCHLORIDE OF MERCURY is converted into a *black* compound. To detect the CHLORIDE OF SILVER in the ammoniacal solution, *nitric acid* must be added in excess, which, by neutralizing the solvent,

TABLE VI.

BEHAVIOUR OF THE MEMBERS OF THE FIRST SECTION WITH THE SPECIAL REAGENTS.

OXIDE OF LEAD (PbO).	OXIDE OF SILVER (AgO).	SUBOXIDE OF MERCURY (Hg_2O).
P 1. $PbCl$ is difficultly soluble in *cold water;* it is much more soluble in *boiling water.* It is precipitated, by HO, SO_3, from its aqueous solutions, as PbO, SO_3, which is insoluble.	Q 1. $AgCl$ is insoluble in *water.*	R 1. Hg_2Cl is insoluble *in water.*
P 2. $PbCl$ is very slightly soluble in NH_4O; the ammoniacal solution becomes turbid after a short time, from the separation of the lead as an insoluble oxychloride ($PbCl, 3\ PbO, + HO$), which is soluble in HO, NO_5; it is therefore easily distinguished from $AgCl$.	Q 2. $AgCl$ is easily soluble in NH_4O. On the addition of any acid it is again precipitated from this solution.	R 2. Hg_2Cl does not dissolve in NH_4O, but becomes altered in colour, the *white chloride* being converted into a *black compound.*

BEHAVIOUR OF THE MEMBERS OF THE SECOND SECTION WITH THE SPECIAL REAGENTS.

PROTOXIDE OF MERCURY (HgO).	OXIDE OF LEAD (PbO).	TEROXIDE OF BISMUTH (BiO).	OXIDE OF CADMIUM (CdO).	OXIDE OF COPPER (CuO).
S 1. HgS is *black;* it is *insoluble* in boiling HO, NO_5, but is easily soluble in aqua regia.	T 1. PbS is *black;* it is *soluble* in boiling HO, NO_5.	U 1. BiS is *black;* it is *soluble* in boiling HO, NO_5.	V 1. CdS is *yellow;* it is *soluble* in boiling HO, NO_5.	W 1. CuS is *black;* it is *soluble* in boiling HO, NO_5.

S 2. Sulphate of the protoxide of mercury is decomposed, in the presence of much water, into an insoluble basic and a soluble acid salt.	T 2. *Sulphuric Acid* precipitates, from solutions of lead, the SULPHATE (PbO, SO_3), which is *insoluble* in water and dilute acids.	U 2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, SULPHATE of BISMUTH being *soluble* in water.	V 2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, the SULPHATE being *soluble* in water.	W 2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, SULPHATE of COPPER being *soluble* in water.
S 3. *Ammonia** produces, in solutions of protoxide of mercury, a WHITE PRECIPITATE ($HgNH_2+HgO$), *insoluble* in an excess of the reagent.	T 3. *Ammonia* throws down, from solutions of salts of lead, white basic salts, which are insoluble in an excess of the reagent.	U 3. *Ammonia* throws down, from solutions of bismuth, the HYDRATE, *insoluble* in an excess of the reagent.	V 3. *Ammonia* precipitates, from solutions of cadmium, the HYDRATE, *soluble* in an excess of the reagent.	W 3. *Ammonia* produces, in solutions of this oxide, a GREENISH BLUE precipitate which *dissolves* with a beautiful azure colour in an excess of the reagent.
S 4. *Carbonate of Ammonia*† behaves in the same way, in solutions of protoxide of mercury, as caustic ammonia.	T 4. *Carbonate of Ammonia* precipitates, from solutions of lead, the CARBONATE (PbO, CO_2) *insoluble* in an excess of the reagent.	U 4. *Carbonate of Ammonia* throws down, from solutions of bismuth, a WHITE BASIC CARBONATE *insoluble* in an excess of the reagent.	V 4. *Carbonate of Ammonia* throws down, from solutions of cadmium, the CARBONATE (CdO, CO_2), *insoluble* in an excess of the reagent.	W 4. *Carbonate of Ammonia* behaves in the same way in solutions of copper as caustic ammonia.

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* The fixed alkalies precipitate all the members of this group from their solutions; the lead precipitate is difficultly soluble in an excess of the reagents; all the rest are insoluble. The precipitate produced by the fixed alkalies, in solutions of the protoxide of mercury, is the yellow hydrate, unless salts of ammonia are present; in that case the precipitate is the same as that produced by ammonia.

† The fixed alkaline carbonates precipitate all the members of this group from their solutions. If added to solutions of copper n the cold, they produce a basic carbonate; but if the solution is boiled, it is converted into the black oxide.

causes the CHLORIDE OF SILVER (if present) to be re-precipitated.

348. *Second section.*—The precipitate produced by the general reagent, after being washed with distilled water until all trace of chlorine* is removed, must be boiled in *dilute nitric acid.* If it all dissolves, with the exception of a light yellow mass of sulphur, PROTOXIDE OF MERCURY is absent; but if, after boiling for some time, the undissolved mass presents a black appearance, it points out the probable presence of that member. Examine the black mass for protoxide of mercury, as directed in paragraph 349. To the acid solution, after it has been filtered from the yellow or black mass, and subsequently evaporated nearly to dryness, so as to remove the greater part of the free acid, must be added a little water, and then a few drops of *dilute sulphuric acid,* which will precipitate the LEAD as sulphate after the lapse of a longer or shorter time; the solution must therefore be allowed to stand some time before ammonia is added. *Ammonia* being added in excess to the filtrate, throws down the BISMUTH.† The filtrate from the ammonia precipitate, or the solution with which that reagent has failed to give a precipitate, is divided into two parts, which we shall call A and B.

A. The A portion is acidulated with acetic acid and tested for COPPER, if the presence of that metal has not been already manifested by the blue colour of the ammoniacal solution, by adding to it *ferrocyanide of potassium,* if *copper is present,* a brownish-red coloured precipitate will be produced, if *that metal is absent,* the colour of the solution will not be altered by the reagent.

B. The B portion when *copper* is absent is examined for CADMIUM in the following manner:—Sulphide of ammonium is added to the ammoniacal fluid, and if it produces a *yellow precipitate*, cadmium is present.

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* The removal of the chlorine is ascertained by the wash-water giving no precipitate on the addition of a few drops of nitrate of silver.

† The precipitate by ammonia must be tested for bismuth by dissolving the washed precipitate in a little dilute hydrochloric acid, and evaporating until only a drop or two of the liquid remains, and then pouring it into a large test-tube filled with distilled water (consult par. 365).

When *copper is present*, the B portion is examined for CADMIUM in the following manner:—Evaporate along with a small quantity of dilute sulphuric acid to dryness and ignite, continuing the ignition until the ammoniacal salt is expelled; then add a *concentrated* solution of sesquicarbonate of ammonia, and boil for a short time, *if no precipitate* is produced, *cadmium* is absent. *If a precipitate is produced*, wash with the solution of the sesquicarbonate of ammonia until all the copper is removed; then dissolve the residue in a little diluted hydrochloric acid, and afterwards add ammonia in excess, and finally *one* drop of sulphide of ammonium; if a *yellowish precipitate** is produced on the addition of the sulphide of ammonium, CADMIUM is present.†

349. If a black residue remain after boiling the mixed sulphides in nitric acid, it must be collected upon a filter, to separate it from the other members, and specially examined for protoxide of mercury by one of the two following methods:—1st. After having dried the black mass thoroughly in a water bath, mix it with dry carbonate of soda, and proceed with the examination for mercury in the way described in paragraph 321. 2nd. Dissolve the black mass in as *small a quantity* of AQUA REGIA *as possible*, then add ammonia in slight excess, and then a slight excess of hydrochloric acid; examine

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* The reason for recommending the addition of only one drop of sulphide of ammonium is this—a small quantity of copper frequently remains undissolved by the carbonate of ammonia, in such a case, if only a drop of sulphide of ammonium be added, the cadmium, if present, will be first precipitated; whereas, if more sulphide of ammonium were added, the copper would also be precipitated, and consequently obscure the cadmium. When the colour of the precipitate produced by sulphide of ammonium is black or of a doubtful colour, it must, after being washed, be dissolved in nitric acid, the solution must be evaporated to dryness, and the residue treated as before with the concentrated solution of sesquicarbonate of ammonia, &c.

† For other methods for the separation of cadmium and copper see par. 376.

the solution, thus prepared, for mercury by means of copper wire, in the way described at par. 361.

350. *The following precautions must be attended to in analyzing this group:*—The means, both for separating and detecting the members of the first section, are so simple and positive, that no difficulty will be experienced by the student. It may, nevertheless, be as well to observe, that chloride of lead ought to be completely removed, before ammonia is added; for if it is not, a *white residue*, which is nothing more than chloride of lead, may remain after the addition of ammonia, when mercury is absent, which may perplex the student. And if the chloride of lead be not completely removed before the addition of ammonia, the ammoniacal solution will appear turbid, owing to the separation of an insoluble basic salt of lead: this will not, however, interfere with the test for silver, since it (the basic salt of lead) redissolves upon the addition of nitric acid. The difficulties which occur in examining the second section will be easily overcome by a little attention. Many erroneous conclusions will be formed if the simple yet necessary precaution of washing the sulphuretted hydrogen precipitate be neglected; because a small quantity of the hydrochloric acid employed to precipitate the first section, being left behind, will be converted, on the addition of nitric acid, into aqua regia, which, by dissolving the protosulphide of mercury, may cause that member to be overlooked; and should the mercury thus pass into solution, a compound of that metal will be precipitated on the addition of ammonia, which may be mistaken for bismuth. The precipitate must therefore, before it is treated with nitric acid, be washed with water until the wash-water, acidulated with nitric acid, gives no precipitate with nitrate of silver. It is difficult to free the mass of sulphur, which separates on the addition of nitric acid, entirely from some of the undecomposed sulphides; and which, by communicating to it a black appearance, might lead to the belief that protoxide of mercury was present, even in the absence of that member. An experienced eye can generally distinguish between this mixture of undecomposed sulphide and sulphur,

and protosulphide of mercury, the former being light and flocculent, whilst the latter is dense and heavy; but a safe and legitimate conclusion can only be arrived at by examining it specially for mercury. A varying amount of sulphuric acid is always formed by dissolving the sulphides in nitric acid: a portion of the lead will therefore be precipitated as sulphate, and remain behind mixed up with the substance insoluble in nitric acid; it is necessary, on this account, to examine the insoluble mass for this member, if it should not be met with in its proper place. As sulphate of lead precipitates from dilute solutions, and especially from those which contain much free acid, only after the lapse of some considerable time, the solution ought, after the addition of sulphuric acid, to be allowed to stand for a considerable time (an hour) before adding the ammonia. A precipitate will be formed on the addition of ammonia to the nitric solution, if either of these reagents contains a trace of iron, but this precipitate cannot be mistaken for bismuth if the following confirmatory test be applied:—Dissolve the precipitate obtained by ammonia in the least possible quantity of dilute hydrochloric acid, and evaporate just to dryness; redissolve the residue in water containing a drop of hydrochloric acid, and then add a large quantity of water; if a turbidness be produced, bismuth is present.

SPECIAL REMARKS.

351. Oxide of Silver.—The colour of this oxide is brown. It is very soluble in nitric acid; it combines with ammonia, giving rise to a dangerous compound (fulminating silver). Many of the salts of silver are colourless and insoluble. The soluble ones do not affect vegetable colours, and are decomposed at a red heat. Many of them blacken on exposure to light; and they are all decomposed with the precipitation of metallic silver by many metals, such as *zinc*, *iron*, *copper*, &c., and by other *reducing agents*. The principal minerals of this metal are the sulphide (*silver glance* AgS), the chloride (*horn sil-*

ver AgCl), SULPHIDE OF SILVER AND ARSENIC ($3AgS + AsS_3$), and SULPHIDE OF SILVER and ANTIMONY ($3AgS + SbS_3$); SILVER is also met with in the metallic state. It is likewise found in small quantities in most lead and copper ores.

352. When silver compounds, mixed with *carbonate of soda*, are subjected on charcoal to the inner blowpipe flame, brilliant metallic globules are produced, which are not attended with any incrustation.

353. OXIDE OF LEAD.—This oxide is of a yellow or reddish-yellow colour. In commerce it frequently goes under the name of massicot, and when partially fused is called litharge. The hydrated oxide is of a white colour, and it speedily absorbs carbonic acid from the air. The best solvent, both for the oxide and its hydrate, is nitric or acetic acid. The salts of lead are frequently insoluble, and are colourless, if the constituent acids be so. The soluble neutral salts redden litmus paper, and are decomposed at a red heat. The principal minerals of this metal are the SULPHIDE (*galena* or *lead glance* PbS) and the CARBONATE (PbO, CO_2).

354. *Chromate of potash* produces, in solutions of lead, a yellow precipitate of CHROMATE OF LEAD (PbO, CrO_3), soluble in the fixed alkalies, but insoluble in nitric acid.

355. When iodide of potassium is added to a solution of a salt of lead, yellow iodide of lead (PbI) is precipitated, which dissolves on heating the liquid, and is re-precipitated on cooling in *brilliant golden-coloured scales.** The solution of the amorphous iodide may be greatly facilitated by the addition of a small quantity of hydrochloric acid. If the *least trace of bismuth* is present in the lead salt, the re-precipitated scales are *no longer yellow*, but assume a *dark orange* or *crimson* tint, varying in intensity of colour according to the amount of bismuth present. This test for bismuth is of extraordinary delicacy.

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* Iodide of lead is very soluble in solutions of the acetates of soda, potash, and ammonia, even in the cold, forming colourless solutions, from which iodide of potassium, added in excess, precipitates iodide of lead in the crystalline state, although no heat has been applied.

356. When lead compounds, mixed with *carbonate of soda*, are exposed upon charcoal to the inner blowpipe flame, ductile metallic globules are formed, accompanied with an incrustation which is yellow whilst hot, but becomes paler on cooling.

357. SUBOXIDE OF MERCURY.—This oxide is black; it is decomposed by heat, the mercury volatilizing in the metallic state. It forms no hydrate. The salts of the suboxide of mercury, when ignited, volatilize either with or without decomposition. The soluble neutral ones redden litmus paper; some of them are decomposed by much water into soluble acid and insoluble basic salts. The colour of the neutral salts is white, the colour of the basic ones is yellow. They are reduced, like the silver salts, by many metals, such as *zinc*, *iron*, *copper*, &c., and by other reducing agents.

358. To obtain the mercury from the subsalts of this metal, they may be decomposed either by copper or protochloride of tin, or by means of carbonate of soda, in the way described at 361, 362, 363.

359. PROTOXIDE OF MERCURY.—This oxide is obtained in the form of a crystalline mass, nearly black whilst hot (at a red heat it is decomposed and entirely volatilized), but of a light red when cold. Its hydrate is yellow. Both the oxide and its hydrate are soluble in hydrochloric and nitric acid. The salts of the protoxide of mercury, when ignited, volatilize either with or without decomposition. The soluble neutral ones redden litmus paper. The sulphate and nitrate are decomposed in the presence of much water into soluble acid and insoluble basic salts. The metals and other reducing agents which decompose the subsalts act in a similar manner upon the protosalts of this metal.

360. These two oxides differ not only in colour, but likewise in their behaviour with alkalies and hydrochloric acid. The latter reagent is especially applicable for separating them, when they are present in the same solution; as subchloride of mercury *(calomel)* is insoluble, whilst the protochloride *(corrosive sublimate)* is soluble.

361. "Metallic copper, introduced into a solution of mercury, especially after acidification with hydrochloric acid, becomes covered with a white lustrous coating; when moderately heated, the copper regains its original colour, vapours of mercury being evolved: this test is exceedingly delicate. Slips of copper wire, about an inch in length, may be used; they should be cleaned by shaking for a few moments with concentrated nitric acid, and thoroughly washed. Half a dozen such slips should be boiled for three or four minutes in the solution, previously acidulated with hydrochloric acid; they are then well rinsed, dried by pressure between blotting-paper, and heated in a glass tube of one quarter of an inch diameter, constructed so as to allow the passage of a feeble current of air. A coating of minute *globules of mercury* is formed upon the cool part of the tube; these may be united into larger globules by rubbing with a glass rod."—(*Abel and Bloxam.*)

362. If protochloride of tin be added in small quantity to salts of the protoxide of mercury, it reduces them to the state of suboxide, and, as a consequence, white subchloride of mercury precipitates; but if it be added in excess, the salt of mercury (subsalts as well as protosalts) is completely decomposed, metallic mercury being thrown down as a gray precipitate, which may be united into globules by heat and agitation—but most readily by boiling the metallic deposit, after decantation of the supernatant fluid, with hydrochloric acid.

363. "Solid compounds of mercury, mixed with a large excess (at least twelve parts) of *dry carbonate of soda*, and heated in a perfectly dry tube of hard glass, having a diameter of about one quarter of an inch, and expanded into a bulb at one end, furnish minute *globules of metallic mercury*, which are deposited on the cool part of the tube, and may be united into larger globules by rubbing with a glass rod. This test is exceedingly delicate; in order that it may be perfectly successful, the mercury compound should be thoroughly dried (in a water bath), and the carbonate of soda should be ignited immediately previous to use. In order to prevent the sublimation of undecomposed mercury compounds, it is well to cover the mixture in

the bulb-tube with a layer of pure carbonate of soda."—(*Abel and Bloxam.*)

364. The chief mineral of this metal is the PROTOSULPHIDE (*cinnabar*); it is likewise met with in the metallic state.

365. TEROXIDE OF BISMUTH.—This oxide is of a yellow colour; when heated, it acquires, for the time, a deeper tint; it fuses at a red heat. Its hydrate is white. They are both readily soluble in the dilute mineral acids. Most of the salts of bismuth are decomposed at a red heat. They are colourless, provided the constituent acid be so. The soluble neutral salts redden litmus paper, and one distinguishing character which they possess is that of being decomposed by water into soluble acid and insoluble basic salts. This property is exhibited in the most decided manner by the chloride. To employ it as a confirmatory test, dissolve the precipitate in a small quantity of hydrochloric acid, evaporate nearly to dryness, and pour this solution into a large quantity of water. If bismuth be present, a milky turbidness will be produced. This metal is found principally in the native state.

366. *Chromate of potash* throws down from solutions of bismuth the YELLOW CHROMATE. This salt differs from the corresponding one of lead by its solubility in dilute nitric acid, and its insolubility in potash.

367. For detecting bismuth in the presence of lead see par. 355.

368. When compounds of bismuth, mixed with *carbonate of soda*, are exposed on charcoal to the inner blowpipe flame, brittle metallic globules are obtained, attended with a yellow incrustation of oxide of bismuth.

369. OXIDE OF CADMIUM.—This oxide is of a brown or yellowish-brown colour: its hydrate is white. They are both easily soluble in the dilute mineral acids. The salts of cadmium are colourless, provided the constituent acid be so. Most of them are soluble in water. The soluble neutral ones redden litmus paper, and are decomposed at a red heat. This metal occurs only in zinc ores. It is found as SULPHIDE in zinc blende, and as OXIDE or CARBONATE in calamine.

370. When compounds of cadmium, mixed with *carbonate of soda* or other reducing agents, are exposed on charcoal to the inner blowpipe flame, the charcoal becomes covered with a yellow or reddish-yellow incrustation of oxide of cadmium.

371. OXIDE OF COPPER.—This oxide is black; its hydrate is of a light blue colour. They are both readily soluble in the dilute mineral acids. Most of the salts of this metal are soluble in water. The soluble ones redden litmus paper, and are decomposed at a red heat. In their anhydrous state, the salts are white; in their hydrated state, they are of a blue or greenish-blue colour, which their solutions exhibit, even when much diluted.

372. This metal is sometimes found in the native state; but it chiefly occurs in combination with sulphide of iron, constituting the COPPER PYRITES ($Cu_2S+Fe_2S_3$), and in BLUE COPPER ore, or MALACHITE ($2\ CuO,\ CO_2+HO$).

373. Ferrocyanide of potassium throws down, even from dilute solutions of copper, a reddish-brown precipitate of FERROCYANIDE OF COPPER ($2\ Cu,\ Cfy$), which is insoluble in dilute acids, but is decomposed by the fixed alkalies.

374. If bright *metallic iron* be introduced into a solution of a salt of copper, it becomes coated with a red deposit of that metal, provided the solution be neutral or only very slightly acid.

375. When any of the compounds of copper, mixed with *carbonate of soda*, are exposed on a charcoal support to the inner blowpipe flame, METALLIC COPPER is obtained, unaccompanied with any incrustation on the charcoal.

376. The following methods have also been proposed for the *separation* of CADMIUM and copper:—

1st. Method.—Acidify the solution, if it is not acid, with hydrochloric acid; then pass sulphuretted hydrogen through the solution. The two metals, if present, will be precipitated as sulphides; the precipitate must be well washed, and then boiled with dilute sulphuric acid. The sulphide of cadmium is decomposed by the sulphuric acid, sulphate of cadmium being formed, which dissolves—whilst the sulphide of copper is undecomposed and undissolved. Separate the two by filtration, test the filtrate for cadmium by sulphuretted hydrogen; dissolve the sulphide of copper in nitric acid; neutralize with ammonia, acidify with acetic acid, then add ferrocyanide of potassium. This is a good method: the only precaution to be attended to is, that the mixed sulphide must be washed rapidly, so that the sulphide of copper may not become oxidized by exposure to the air. (*Dr. A. W. Hoffman.*)

2nd. Method:—To one portion of the acetic solution add *hydrosulphuric acid* in excess. The formation of a yellow precipitate denotes CADMIUM. If, on account of the presence of copper, the sulphide of cadmium cannot be distinctly recognised, allow the precipitate produced by the hydrosulphuric acid to subside, decant the supernatant fluid, and add to the precipitate a solution of *cyanide of potassium* until the sulphide of copper is dissolved. If a yellow residue is left undissolved, CADMIUM is present; in the contrary case, not. (*Fresenius.*)

377. For a method for detecting very minute quantities of bismuth, arsenic and antimony in metallic copper, see Appendix to Part I.

CHAPTER III.

THE GENERAL PROPERTIES OF THE BASIC GROUPS.

378. It will be seen by consulting the General Table (VII), that some of the reagents produce a precipitate with more than one of the groups; the analysis must therefore be commenced by removing those substances the general reagent of which produces no precipitate with the members of any other group under the same circumstances. Such a course will be adopted, if the reagents are employed in the order observed in the table.

379. FIRST DIVISION OF THE SIXTH GROUP.—The analysis must be commenced by adding to the solution *hydrochloric acid*, which precipitates the members of the first section of the sixth group when they are present. When a precipitate is produced, collect it upon a filter, wash it twice with cold water, and then examine it, according to the first section of Table VI, and par. 347. The wash-water must be collected with the filtrate. *Before adding the hydrochloric acid, consult* pars. 401, 402, and 403.

380. The filtrate from the precipitate produced by hydrochloric acid, or the solution with which that *acid* has failed to give a precipitate, must be examined for *the second division of the sixth and the whole of the fifth group*, in the manner described in the next paragraph.

381. SECOND DIVISION OF THE SIXTH AND THE WHOLE OF THE FIFTH GROUP.*—*Sulphide of hydrogen* gas (hydrosulphu-

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* Gold and platinum are easily detected in the presence of all the metals (paragraph 331); Northcote and Church, in their 'Manual of Analysis,' recommend their separation from the solution, before precipitating the other members of the fifth and the members of the sixth group, by sul

ric acid),[*] must be added to the solution until it *smells strongly* of the gas after it has been shaken and gently warmed for some time; the members of the second section of the sixth, and the members of the fifth group, when present, will be precipitated. When a precipitate is produced, collect it upon a filter and wash it with hot water, until the wash-water is no longer acid to test-paper; the wash-water need not be collected with the filtrate, but may be thrown away.

382. If the FIFTH GROUP *has not to be examined for*, the *washed precipitate* is at once examined according to Table VI and par. 348.

383. When the FIFTH GROUP *has to be examined for*, the *washed precipitate* must be treated with boiling *caustic soda*; the members of the SIXTH GROUP are *insoluble* but the members of the FIFTH are *soluble* in the alkaline solution; if any of the precipitate is insoluble in the soda solution, filter, and treat the *insoluble portion* according to par. 384. *Examine the soda solution for the fifth group according to* par. 385.

384. The portion of the precipitate insoluble in the soda solution must be examined, after it has been well washed, according to Table VI, and par. 348.

385. To the caustic soda solution must be added *hydro-*

phuretted hydrogen; the following is their plan:—The filtrate from the HCl precipitate, or the solution which has failed to give a precipitate, is freed from HO, NO_5 (if present) by one or two evaporations on the water-bath with HCl; to the HCl solution, which ought to be concentrated, a reasonable quantity of NH_4Cl solution is added, the liquid is then well agitated and allowed to rest for some hours; if Pt is present, a yellow crystalline precipitate of $PtCl_2$, NH_4Cl is formed. The filtrate is mixed with a reasonable quantity of a concentrated solution of HO, C_2O_3, and moderately heated for some hours. A precipitate, consisting of yellow spangles or of a brown-yellow sponge indicates Au. The filtrate is then treated with HS.

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[*] If the oxides of silver and lead, and suboxide of mercury, had not to be sought for, we must nevertheless add hydrochloric acid to the solution to render it acid, before adding sulphide of hydrogen, in order to prevent the members of the third and fourth groups from being precipitated by that reagent, and to ensure the complete precipitation of the fifth group.

chloric acid in excess. If a precipitate is produced, on the addition of the acid, the colour of which is *white*, this arises merely from the separation of sulphur, *none of the members of the group being present*; if the precipitate is of a *yellow* or *orange colour*, ANTIMONY, BINOXIDE OF TIN,* and ARSENIC, can only be present. If the colour of the precipitate is *black*, then all the members of the group must be sought for. The analysis of the precipitate, after being well washed with hot water, must be conducted according to the directions given under the fifth group. *Before passing the sulphide of hydrogen gas through the solution consult* pars. 404, 405, and 406.

386. The *filtrate* from the sulphide of hydrogen precipitate, or the *solution* with which it has failed to give a precipitate, must be boiled until every trace of sulphide of hydrogen is expelled. To ascertain when all the gas is expelled, hold a piece of bibulous paper, moistened with a solution of some soluble salt of lead, over the boiling liquid: when the lead-paper does not alter in colour, all the sulphide of hydrogen is expelled. If boiling the liquid causes a separation of sulphur, the solution, after the sulphide of hydrogen is expelled, must be filtered to free it from sulphur—the liquid must then be examined for the *fourth group* as directed in the next paragraph.

387. THE FOURTH GROUP.—Before adding to the solution the general reagent for the fourth group, the solution must be tested for protoxide of iron, and it may also be tested for the peroxide, for this purpose, to a small portion of the solution must be added ferricyanide of potassium,† and to another small portion‡ ferrocyanide of potassium (if copper is present it will be better to employ a soluble sulpho-cyanide), observing the precautions mentioned in par. 246. When *protoxide* of iron is present the remainder of the solution to which no ferro- or ferri-cyanide of potassium has been added, must be boiled in an

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* The colour of protosulphide of tin is a blackish brown.

† Ferro- and ferri-cyanide of potassium precipitate a great many of the metallic oxides, besides the iron oxides, but with no other oxides but the iron oxides do they give *blue* precipitates.

‡ When the sixth and fifth groups have been examined for, and prot-

evaporating dish with a few drops of nitric acid, until all the iron is converted into sesquioxide, which is accomplished when a drop of the solution does not give a blue colour with ferricyanide of potassium. When *protoxide* of iron is not present the solution does not require to be boiled with nitric acid, but it may at once be examined for the fourth group as directed in the next paragraph.

388. *Chloride of ammonium and ammonia* must then be added to the solution; the ammonia must be added until the solution, after it has been well shaken, smells of the volatile alkali. Warm the solution after the addition of the ammonia; and when a precipitate is produced, showing the presence of one or all of the members of the fourth group, collect it upon a filter, wash it with hot water until the wash-water does not turn red test-paper blue; examine it then according to Table IV and par. 226. *Before adding the chloride of ammonium and ammonia, consult* pars. 407, 408, and 409.

389. The *filtrate* from the precipitate produced by ammonia, or the *solution* with which that reagent has failed to give a precipitate, must be examined for the THIRD GROUP according to the method described in the next paragraph.

390. THIRD GROUP.*—*Sulphide of ammonium*† must be added

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oxide of iron is found to be present, it is necessary to test the *original* solution with ferro- and ferri-cyanide of potassium in order to ascertain in what state of oxidation the iron exists in the solution; because sulphuretted hydrogen reduces persalts of iron to the state of protosalts, therefore iron will always be found in the state of protoxide in its solutions after sulphuretted hydrogen has been added in excess.

[*] Although protoxide of iron belongs, on account of its general porperties, to this group, we have placed it in the special table of the fourth group; because, in separating the groups, it is converted by nitric acid into sesquioxide—a member of the fourth group: we have thought it advisable, therefore, to contrast its special properties with those of the fourth.

[†] When the student does not look for the members of the three previous groups, viz. the sixth, fifth, and fourth, he must, before adding sulphide of ammonium to the solution, add chloride of ammonium and ammonia: in other words, he must add them to the solution which he has to examine

TABLE VII.—BEHAVIOUR OF THE BASIC GROUPS

FIRST GROUP.	SECOND GROUP.		THIRD GROUP.
POTASH (KO), **SODA** (NaO), **AMMONIA** (NH_4O).	*First Subdivision.* **BARYTA** (BaO), **STRONTIA** (SrO), **LIME** (CaO).	*Second Subdivision.* **MAGNESIA** (MgO)	**OXIDE OF MANGANESE** (MnO), **OXIDE OF ZINC** (ZnO), **OXIDE OF COBALT** (CoO), **OXIDE OF NICKEL** (NiO), **PROTOXIDE OF IRON** (FeO).
1. **HYDROCHLORIC ACID** *does not* precipitate the members of this group from their solutions, because *their Chlorides are soluble.*	1. **HYDROCHLORIC ACID** *does not* precipitate the members of this group from their solutions, because *their Chlorides are soluble.*		1. **HYDROCHLORIC ACID** *does not* precipitate the members of this group from their solutions, because *their Chlorides are soluble.*
2. **HYDROSULPHURIC ACID** *does not* precipitate the members of this group, either from their neutral acid or alkaline solutions, because *their Sulphides are soluble.*	2. **HYDROSULPHURIC ACID** *does not* precipitate the members of this group, either from their neutral acid or alkaline solutions, because *their Sulphides are soluble.*		2. **HYDROSULPHURIC ACID** *does not* precipitate the members of this group from their *acid* solutions, because *their Sulphides* are soluble in *dilute acids,* even in the cold.
3. **AMMONIA** *does not* precipitate either of the other two members of the group.	3. **AMMONIA** *does not** precipitate the members of this division from their solutions.	3. **AMMONIA** *precipitates* Magnesia *partly* from its solutions as *Hydrate* (MgO, HO); the presence of *Salts of Ammonia prevents** the precipitation *altogether.*	3. **AMMONIA** *precipitates* the members of this group as *Hydrates.* In an excess of the reagent, the Hydrates of Zinc, Nickel, and Cobalt are *readily soluble,* but the Hydrates of Manganese and Protoxide of Iron are *insoluble;* but the presence of *Salts of Ammonia prevents* the precipitation of the *Manganese* and *Oxide of Iron.*
4. **SULPHIDE OF AMMONIUM** *does not* precipitate the other two members of this group from their solutions, because *their Sulphides are soluble.*	4. **SULPHIDE OF AMMONIUM** *does not* precipitate the members of this group from their solutions, because *their Sulphides are soluble.*		4. **SULPHIDE OF AMMONIUM** *precipitates* all the members of this group from neutral and alkaline solutions, as *Sulphides.*
5. **CARBONATE OF AMMONIA** *does not* precipitate either of the other two members of this group from their solutions.	5. **CARBONATE OF AMMONIA** *precipitates* the members of this division from their solutions as *Carbonates;* the presence of *Salts of Ammonia does not interfere* with the precipitation.	5. **CARBONATE OF AMMONIA** *precipitates* Magnesia *only partly,* and the presence of *Salts of Ammonia prevents* the precipitation *altogether.*	5. **CARBONATE OF AMMONIA** *precipitates* all the members of this group; but they *are all,* with the exception of Manganese and Oxide of Iron, *readily soluble* in an *excess* of the reagent.
6. **PHOSPHATE OF SODA** *does not* precipitate either of the other two members of this group from their solutions.	6. **PHOSPHATE OF SODA** *precipitates* the members of this division from their neutral and alkaline solutions, as *Phosphates.*	6. **PHOSPHATE OF SODA** *precipitates* Magnesia from its neutral and alkaline solutions, as *Phosphate;* violent agitation promotes the formation of the precipitate. The precipitate is more soluble in *hot* than *cold* water.	6. **PHOSPHATE OF SODA** *precipitates* the members of this group from their neutral solutions, as *Phosphates.*

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* The phosphates and oxalates of baryta, strontia, and lime, and phosphate of magnesia, are soluble in dilute mineral acids, but insoluble in water and the alkalies; consequently, when their acid solutions are rendered neutral or alkaline by ammonia, *these salts* are precipitated; therefore when baryta, strontia, and lime are in combination with phosphoric and oxalic acids, and when magnesia is in combination with phosphoric acid, they are precipitated in combination with these acids by ammonia, from their acid solutions, along with the members of the fourth group.

FOURTH GROUP.	FIFTH GROUP.	SIXTH GROUP.	
		Second Subdivision.	*First Subdivision.*
Alumina (Al_2O_3), Sesquioxide of Chromium (Cr_2O_3), Sesquioxide of Iron (Fe_2O_3).	Arsenious Acid (AsO_3), Arsenic Acid (AsO_5), Teroxide of Antimony (SbO_3), Oxide of Tin (SnO), Binoxide of Tin (SnO_2), Teroxide of Gold (AuO_3), Binoxide of Platinum (PtO_2).	Oxide of Lead (PbO), Protoxide of Mercury (HgO), Teroxide of Bismuth (BiO_3), Oxide of Cadmium (CdO), Oxide of Copper (CuO).	Oxide of Silver (AgO), Suboxide of Mercury (Hg_2O), Oxide of Lead (PbO).
1. Hydrochloric Acid *does not* precipitate the members of this group, because *their Chlorides are soluble.*	1. Hydrochloric Acid *does not* precipitate the members of this group, because *their Chlorides are soluble.*	1. Hydrochloric Acid *does not* precipitate the members of this division of the group because *their Chlorides are soluble.*	1. Hydrochloric Acid *precipitates* the members of this division of the group, because *their Chlorides are insoluble.* Chloride of Lead is slightly soluble in water; it is more soluble in hot than cold water.
2. Hydrosulphuric Acid *does not* precipitate any of the members of this group from their acid solutions, because *Sulphide of Iron* is readily soluble in acids, and the *Sulphides of Aluminum* and Chromium are not formed in the humid way.	2. Hydrosulphuric Acid *precipitates* all the members of this group from their acid solutions, as *Sulphides.*	2. Hydrosulphuric Acid *precipitates* all the members of this group from their neutral alkaline and acid solutions, as *Sulphides.*	
3. Ammonia, *even in the presence of its Salts*, precipitates the members of this group as *Hydrates*,[*] which an *excess* of the reagent *does not* redissolve.	3. Ammonia *precipitates* some of the members of this group.	3. Ammonia precipitates the members of this group; but *in an excess* of the reagent, the *oxides of Silver, Cadmium,* and *Copper* redissolve readily; the *rest* are *insoluble* in an excess of the reagent.	
4. Sulphide of Ammonium *precipitates* all the members of this group from neutral and alkaline solutions; Sesquioxide of Iron, as *Protosulphide;* Alumina and Sesquioxide of Chromium, as *Oxides.*	4. Sulphide of Ammonium, *if added in excess,* does not precipitate the members of this group from their solutions, because *their Sulphides* are soluble in the *Alkaline Sulphides.*	4. Sulphide of Ammonium *precipitates all* the members of this group from their neutral and alkaline solutions, as *Sulphides.*	
5. Carbonate of Ammonia *precipitates* all the members of this group from their solutions as Oxides; an *excess* of the reagent *does not* redissolve them.	5. Carbonate of Ammonia precipitates *some* of the members of this group, as *Oxides.*	5. Carbonate of Ammonia *precipitates* all the members of this group from their solutions; and an excess of the reagent *does not* redissolve them, with the *exception* of Copper.	
6. Phosphate of Soda *precipitates* the members of this group from their neutral solutions, as *Phosphates.*	6. Phosphate of Soda *precipitates* some of the members of this group from their neutral solutions, as *Phosphates.*	6. Phosphate of Soda *precipitates* the members of this group from their neutral solutions, as *Phosphates.*	

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[*] When phosphate of iron and phosphate of alumina are present in a solution, they are precipitated as Phosphates, and not as Hydrates, by ammonia.

to the solution, the liquid must afterwards be shaken and gently heated for some time. If any of the members of the third group are present, a precipitate will be produced by the sulphide of ammonium. *When a precipitate is produced*, collect it upon a filter, and examine it according to Table III and par. 198. Before filtering the whole of the solution, add to that portion of the liquid which has been filtered, a little more sulphide of ammonium; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, re-filter, and again test the filtrate with sulphide of ammonium. If the sulphide of ammonium causes no precipitate in the filtered liquid, proceed with the filtration, as the group has been completely precipitated. *Before adding sulphide of ammonium to the solution consult* pars. 410, 411, 412.

391. If the *filtrate* from the sulphide of ammonium precipitate, or the *solution* with which it has failed to give a precipitate, has become, from the addition of the sulphide of ammonium, of a *dark-brown colour*, the filtrate or solution must be evaporated and then acidified with hydrochloric acid, and filtered as directed in par. 412. *Ammonia* in excess must be added to the filtrate which must then be examined for the SECOND GROUP according to par. 393.

392. If the *filtrate* from the sulphide of ammonium precipitate, or the *solution* with which it has failed to give a precipitate, has *not altered in colour* by the addition of the sulphide of ammonium, it can at once be examined for the SECOND GROUP as directed in the next paragraph.

393. FIRST DIVISION OF THE SECOND GROUP.—*Carbonate of ammonia*[*] must be added to the solution; the solution must then be gently warmed for some time, *but not boiled.* If

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for the members of the third group, if they (*i. e.* chloride of ammonium and ammonia) have not been added in the previous course of the analysis. The chloride of ammonium is added, to prevent the precipitation of magnesia by ammonia.

[*] When the student does not look for the members of the four previous groups, viz., the sixth, fifth, fourth, and third, he must, before adding the carbonate of ammonia to the solution, add chloride of ammonium and ammonia: in other words, he must add them to the solution which he has

one or all of the members of this division are present, a precipitate will be produced by the carbonate of ammonia, especially after warming the solution. *When a precipitate is produced*, collect it upon a filter and wash it with hot water, and afterwards examine it according to Table II and par. 165.

Before filtering the whole of the solution, add to that portion of the liquid which has been filtered a little more carbonate of ammonia; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, refilter, and again test the filtrate with carbonate of ammonia. If the carbonate of ammonia causes no precipitate in the filtered liquid, proceed with the filtration, as the group has been completely precipitated. *Before adding the carbonate of ammonia, consult pars.* 413 and 414.

394. The *filtrate* from the precipitate produced by carbonate of ammonia, or the *solution* with which that reagent has failed to give a precipitate, must be examined for MAGNESIA and the FIXED ALKALIES as directed in the next paragraph.

395. MAGNESIA AND THE FIXED ALKALIES.—The solution, which has to be examined for magnesia and the fixed alkalies, must be divided into two parts, which we shall call A and B.

396. The A portion may be employed for the examination of *magnesia*, for this purpose we must add to the solution, which must be quite cold; *phosphate of soda* and also ammonia, if this latter reagent is not already present in the solution, the liquid after the addition of the reagent ought to be shaken very violently; and if, after time (one or two hours) has been allowed for the formation of the precipitate, *there is*

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to examine for the members of the second group, if they (*i. e.* chloride of ammonium and ammonia) have not been added in the previous course of the analysis. The chloride of ammonium is added to prevent the precipitation of the magnesia by the carbonate of ammonia; any ammoniacal salt may be employed, the acid of which forms no insoluble compound with magnesia or the other members of the group. The carbonate of ammonia employed being generally a sesquicarbonate, a portion of the alkaline earths is apt to be dissolved by the excess of carbonic acid. The ammonia is added to prevent this: it does so by converting the sesquicarbonate into a neutral carbonate.

no precipitate MAGNESIA *is absent.* If *there is a precipitate,* MAGNESIA *is present. Before adding the phosphate of soda, consult* par. 415.

397. The B portion may be employed for the examination for the *fixed alkalies;* and as magnesia does not alter or modify in the least the colours which *potash* and *soda* impart to the flame, it is not necessary in examining for the fixed alkalies by the blowpipe flame, to separate magnesia if it is present, from the solution. The B portion, after the expulsion of the ammoniacal salts, must be examined for the fixed alkalies, as directed in next par., attention being paid also to the directions in par. 399, when *strontia is present.*

398. If the first division of the SECOND and previous groups have been examined for—the B solution ought, before it is examined for the fixed alkalies, to be evaporated to dryness and ignited to expel the ammoniacal salts which have been added in the course of the analysis. The expulsion of the ammoniacal salts is necessary, as they frequently contain organic matter and all organic substances which burn with the separation of carbon, give, like potash, a *violet colour* to the flame. The ignition ought to be continued until all fuming ceases, the lamp is then removed, and when the vessel is cold as much *boiling water* as would fill a small-sized thimble should be poured into the vessel, in order to dissolve the fixed alkalies if they are present. The liquid must then be filtered through a very small filter, and the filtrate examined for the *fixed alkalies* according to par. 130; par. 132 ought to be consulted.

399. When a precipitate has been produced by carbonate of ammonia, one drop of dilute sulphuric acid ought to be added to the B solution before it is evaporated and ignited. The acid is added to remove the minute quantity of strontia if present, which remains unprecipitated by carbonate of ammonia, as strontia imparts to the flame a colour very similar to that produced by potash.

400. AMMONIA. A portion of the *original* solution must be examined for ammonia according to par. 129.

PARTICULAR OBSERVATIONS REGARDING THE PRECIPITATES PRODUCED BY THE GENERAL REAGENTS, AND THE PRECAUTIONS TO BE ATTENDED TO IN EXAMINING THE SOLUTIONS.

401. *Precautions to be attended to in examining for the first section of the Sixth Group.*—Before adding hydrochloric acid to the solution under examination, it is necessary to ascertain, by test-papers, whether the solution is acid, neutral, or alkaline. When it is one of the two former, a few drops of the acid will generally be sufficient; if alkaline, the acid must be added until it is decidedly in excess. When a precipitate is produced, add the acid, drop by drop, until it ceases to increase; then add a few drops more, shake the mixture, and filter. When no precipitate is produced, a few drops of the acid will in most cases be sufficient, since our only object in adding it then is to acidify the solution, in order to prevent the precipitation of the members of the third and the members of the fourth group by sulphide of hydrogen. *When an evolution of gas takes place on the addition of the hydrochloric acid, consult* par. 419.

402. As oxide of silver is not precipitated, under certain circumstances, by hydrochloric acid—and as a precipitate may be produced on the addition of hydrochloric acid, in the absence of the oxides of silver, lead, and suboxide of mercury—it is requisite to notice, 1st, the substances which interfere with the precipitation of the oxide of silver; 2nd, the substances which may be precipitated, and under what condition the precipitation takes place. 1st. When protonitrate of mercury is present in the solution, oxide of silver, if present, will not be precipitated by the hydrochloric acid, because chloride of silver is soluble in a solution of protonitrate of mercury, especially if the solution is hot and concentrated: on the addition of water and cooling, the solution may deposit shining yellowish-white crystals, which are pure chloride of silver. When protonitrate

of mercury is suspected to be present, acetate of ammonia ought to be added to the solution after the addition of the hydrochloric acid, as this ensures the complete precipitation of the chloride of silver. 2nd. The precipitate[*] may be occasioned by the presence of some salt of antimony or bismuth, as the chlorides of these metals are decomposed by much water into soluble acid and insoluble basic salts. This precipitate[†] may also arise from the presence of some substance insoluble in water, but soluble in the caustic, carbonated, or sulphuretted alkalies, or in an alkaline cyanide—for example, phosphate of alumina, or alumina dissolved in caustic soda, sulpharsenious acid dissolved in carbonate of ammonia, tersulphide of antimony dissolved in an alkaline sulphide, cyanide of nickel dissolved in an alkaline cyanide; or the precipitate may be due to silicic acid, some alkaline silicate being present. If the precipitate is due either to antimony or bismuth, it will redissolve on the addition of a few drops more of hydrochloric acid. When silicic acid is the substance thrown down, the precipitate will appear very gelatinous, and will remain undissolved on the further addition of acid; a fresh portion of the original solution must therefore be acidulated with nitric acid, and evaporated to dryness to render the silicic acid insoluble; the ignited mass may then be digested with dilute nitric acid, and filtered.[‡] The analysis of the filtrate must then be conducted in the regular way, by adding to it hydrochloric acid, &c. If the precipitate should be due to the presence of any of the other substances, a fresh portion of the original solution ought to be taken, and nitric acid added to it until it is decidedly acid. If the precipitate does not disappear on the addition of the acid, the solution ought to be warmed; if this should fail to dissolve the precipitate, it must be collected upon a filter, and examined as a substance insoluble in water and acids (*see* 719). The analysis of the solution or filtrate must then be conducted in the regular way, by adding to it hydrochloric acid, &c.

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[*] If the hydrochloric acid employed contain a trace of sulphuric acid, and baryta be present in the fluid under examination, a slight trace of insoluble sulphate of baryta will be formed, which may be distinguished by the difficulty experienced in separating it from the fluid by filtration.

[†] Hydrochloric acid precipitates, of the inorganic acids, boracic acid; and of the organic acids, benzoic and uric acids, if the solution is very concentrated. The two former are dissolved by hot water, and the uric acid by heating with nitric acid.

[‡] The precipitate left upon the filter must be examined for silicic acid according to the method described under the head of that acid (see par. 508).

403. As the chlorides of lead, silver, and subchloride of mercury, are very heavy, they easily separate from the solution; there is therefore no need to warm the fluid to effect this object. Indeed it would be disadvantageous to do so, as a portion of the subchloride of mercury would be converted into protochloride, and the greater portion, if not all, the chloride of lead would be dissolved.

404. *Precautions to be observed in examining for the second section of the Sixth and the whole of the Fifth Group.*—Before passing sulphide of hydrogen through the solution it will be necessary to dilute it with water, if it be very acid, as many sulphides will not readily precipitate from very acid solutions. Should the liquid, on being diluted, become turbid, it arises from the presence of some salt of antimony or bismuth. A few drops of acid will redissolve this precipitate. Arsenic acid is precipitated, with very great difficulty, by sulphide of hydrogen. When this substance is present, the addition of sulphurous acid,* assisted by a gentle degree of heat, reduces it to a lower oxide (arsenious acid). This must be done before passing sulphide of hydrogen through the solution; for not only is the arsenic acid precipitated with difficulty, but if oxide of zinc is also present in the solution, the precipitate produced by the sulphide of hydrogen is not pure sulpharsenic acid, but a compound of that acid and sulphide of zinc, having the following composition (ZnS, AsS_5)—so that if the oxide of zinc and arsenic acid were present in equivalent proportions, all the

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* If baryta, strontia, or oxide of lead, be present, the sulphurous acid will give rise to a precipitation of these oxides, as sulphates; the precipitate should be collected upon a filter, washed, dried, and then examined as a substance insoluble in water and acids, according to 719.

zinc would be precipitated along with the arsenic acid by sulphide of hydrogen. If, however, the arsenic acid be first reduced, by means of sulphurous acid, to the state of arsenious acid, then no sulpharsenic acid is precipitated, but only sulpharsenious acid (AsS_3); and sulphide of zinc is not precipitated along with this last acid.

405. If, on the addition of hydrosulphuric acid, no precipitate be produced, it proves the absence of the remaining members of the sixth and all the members of the fifth group. If a precipitate be produced, the colour of which is white,* this likewise proves the absence of these groups, as the white precipitate is merely due to a separation of sulphur, occasioned by the reduction of some higher oxide to a lower degree of oxidation. If the colour of the solution, originally orange or yellow, change to a green, after the gas is passed through it, the separation of sulphur is due to the reduction of chromic acid to the state of sesquioxide of chromium; the white sulphur suspended in the green solution frequently perplexes the student, as it appears at first like a green precipitate. If the separation of sulphur be not attended with any change in colour, it is (probably) attributable to the reduction of the sesquioxide of iron to the state of protoxide: chromic acid and sesquioxide of iron being both found in their lowest degree of oxidation, after sulphide of hydrogen or any reducing agent has been added to their solutions.

406. If on the first transmission of sulphide of hydrogen through the solution a *white* precipitate be formed, which, on a further addition of the reagent, acquires *an orange colour*, and becomes finally *black*, it points out that some salt of the protoxide of mercury is present. If the precipitate, on its first

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* If nitric acid be present in the solution, a thick tenacious yellow mass of sulphur will separate, occasioned by the decomposition of the sulphide of hydrogen by the acid. When such is the case, the gas has to be passed through the solution for some time before its characteristic odour will be imparted to the liquid, showing that a sufficient quantity has been added. Chloric acid and free chlorine decompose sulphide of hydrogen in the same way as nitric acid.

formation, assumes a red or brownish-red colour, and becomes finally black, it indicates the probable presence of some salt of lead.

407. *Precautions to be observed in examining for the Fourth Group.*—If the sulphide of hydrogen were not expelled before boiling the solution with nitric acid, the latter would give rise, by oxidation of the sulphur, to sulphuric acid, which would precipitate baryta and strontia, and possibly lime, as sulphates, if they were present. Even when nitric acid has not to be added to the solution, no oxide of iron being present, it is necessary to expel the sulphide of hydrogen before adding ammonia, otherwise sulphide of ammonium would be formed when the ammonia was added, and consequently the third as well as the fourth group would be precipitated. When the solution is very acid, no chloride of ammonium need be added, as a sufficient amount of ammoniacal salt will be formed on the addition of the ammonia.

408. When much sesquioxide of chromium is present, a small quantity will frequently dissolve in the ammonia, and will impart to the fluid a puce-red tint. When this occurs, it is difficult to remove the last traces of chromium from the solution. If warming the solution fail, it is better to disregard it; for if the solution were evaporated to effect the object, a greater or less quantity of the oxides of manganese, nickel, and cobalt, if they were present, would be precipitated.

409. The precipitate produced by ammonia may consist, in addition to the members of the fourth group, of the following salts:—Alumina, sesquioxide of chromium, sesquioxide of iron, baryta, strontia, lime, and magnesia, when in combination with phosphoric acid; and baryta, strontia, and lime, when in combination with oxalic acid. When the student looks for acids as well as bases, he must examine the precipitate produced by ammonia, according to Table V. Baryta, strontia, and lime, when in combination with hydrofluoric and boracic acids, may also be precipitated by ammonia in minute quantities; but as a sufficient quantity of the bases will always remain in solution, and be precipitated in their proper place, and as the acids

will be found in the examination for acids, we have not included these salts in the table.

410. *Precautions to be observed in examining for the Third Group.*—If chromic acid and baryta are both present in a solution, a substance insoluble in acids is sometimes found on dissolving the precipitate produced by ammonia, or that produced by sulphide of ammonium; the insoluble substance is sulphate of baryta. A sulphur acid appears to be formed when chromic acid is reduced by sulphide of hydrogen, which becomes converted into sulphuric acid after some time.

411. The precipitate produced by sulphide of ammonium is very difficult to filter; the filtrate will frequently come through the filter *turbid* for some time; there is no remedy for this but to pass it through the filter until it is perfectly clear. The student must not mistake between a *turbid filtrate* and one which is *perfectly clear but coloured.* A filtrate can only remove what is held in suspension by a liquid, as in the first case; it cannot remove what is dissolved, as in the second case; when the filtrate is coloured, consult the next paragraph. The precipitate must be carefully washed with water containing a little sulphide of ammonium, in order to prevent the precipitated sulphides from oxidizing. If the wash-water comes through of a deep-brown colour, it must be treated as directed in the next paragraph.

412. If the filtrate from the sulphide of ammonium precipitate be of a very dark-brown colour, it is occasioned by the presence of nickel, the sulphide of that metal being slightly soluble in sulphide of ammonium. When a considerable portion of this substance has passed into solution, the filtrate, and likewise the wash-water if it is dark-coloured, must be evaporated until the excess of sulphide of ammonium is expelled; the solution is then acidified with dilute hydrochloric acid, and the black precipitate which separates on the addition of the acid collected upon a filter, and examined with that previously obtained.

413. *Precautions to be observed in examining for the first division of the Second Group.*—After the addition of the carbo-

nate of ammonia, the solution should be heated gently, but not boiled, since the chloride of ammonium might then decompose and dissolve the carbonates of the alkaline earths.

414. Although carbonate of ammonia does not precipitate completely baryta, strontia, and lime from their solutions, especially when the quantity of the salts of ammonia present is considerable, it is sufficiently exact for all ordinary qualitative purposes. "The separation is never perfect, owing to the solvent action which salts of ammonia exercise, more especially upon carbonate of baryta and lime; indeed, minute traces of baryta and lime can rarely be precipitated in this manner. Baryta is separated the most completely by sulphuric acid or a sulphate; lime, by oxalate of ammonia, in presence of ammonia and some chloride of ammonium; strontia, same manner as lime, or by ammonia and carbonate of ammonia in presence of chloride of ammonium."

415. *Precautions to be observed in examining for the second division of the Second Group.*—If the solution has become very dilute during the course of the analysis, it will render the detection of the magnesia more certain, if, before adding the phosphate of soda, the solution is concentrated. In any case, time must be allowed for the formation of the precipitate, the solution must be quite cold when the reagent is added, and after the addition of the reagent the solution must be frequently shaken; as phosphate of magnesia and ammonia is more insoluble in water containing ammonia than in pure water it is necessary to keep ammonia in excess.

CHAPTER IV.

THE GENERAL PROPERTIES OF THE ACIDS.

416. ALL acids belong to one of two grand classes, which are distinguished by the terms *Organic* and *Inorganic*. The striking characteristic of the organic class of acids is the separation of charcoal which attends their decomposition by heat, along with the conversion of the bases with which they are combined (if alkalies or alkaline earths) into carbonates.

417. Acids do not admit of that accurate classification into groups which is the case with bases, many of them being members of more than one group.

INORGANIC ACIDS.

418. The inorganic acids treated of in the present work are divided into six groups.

419. *First Group.*—The acids in this division are not only gaseous in their free state, but their affinity for bases is likewise feeble; their salts are therefore decomposed by most acids, the decomposition being attended with *effervescence*, owing to the liberated acid assuming the gaseous state. On this account they are always discovered at the very commencement of an analysis; for an evolution of gas must take place, when hydrochloric acid is added to test for the first section of the sixth group of bases, if these acids are present. The evolved gas must be examined—1, By the smell; 2, by paper moistened with a solution of acetate of lead; 3, by placing the thumb on the mouth of the test-tube, so that the gas may accumulate, and finally decanting it (taking care not to allow any of the liquid to pass over along with it) into another test-

tube half filled with *lime-water*. If, on agitating the liquid, a precipitate be formed, CARBONIC ACID is present.* The special properties just alluded to will be found detailed in the respective paragraphs of these acids.

420. Positive proof will thus be afforded of the presence or absence of carbonic and hydrosulphuric acid. Hydrocyanic acid may, especially in the presence of much hydrosulphuric acid, be overlooked in this way. The methods to be employed for its detection in all cases will be afterwards stated.

421. *Second Group.*—The acids contained in this group are detected in testing for the bases. ARSENIOUS and ARSENIC ACID, being precipitated by hydrosulphuric acid, are classed amongst the bases; whilst the remaining acid is converted into a lower oxide, sesquioxide of chromium, which is one of the members of the fourth group of bases. The change of colour attending this decomposition is so characteristic, that it cannot be overlooked by the most inexperienced student. The only thing which can cause the least difficulty or perplexity is the mistaking a green solution, with a light-coloured precipitate suspended in it, for a green precipitate.

422. *Third Group.*—It will be seen by referring to the table that some of the acids already noticed form a part of this group. The examination is commenced by adding to a portion of the original solution *chloride of barium;* if a precipitate be formed which is not entirely soluble in hydrochloric acid, SULPHURIC ACID is present; filter off from the insoluble sulphate of baryta, and to the filtrate add ammonia; if no precipitate ensue, the other acids (boracic acid excepted) in the group cannot be present. Borate of baryta is soluble in ammoniacal salts, from which solution it is not precipitated on the addition of ammonia.† Arseniate and arsenite of baryta are likewise

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* Carbonic acid is very soluble in a solution containing phosphate of soda; when this salt is present, examine for carbonic acid according to the method described in par. 454.

† Oxalate of baryta and fluoride of barium are soluble in ammoniacal salts, though in a less degree than borate of baryta, and, like this latter salt, they are not precipitated from this solution by ammonia; oxalic acid

soluble in ammoniacal salts, from which solutions ammonia fails to precipitate them, but their presence or absence will have been determined already. If any base is present which is precipitated by ammonia, it must be removed before we can employ the alkali for pointing out whether any other acid is present but sulphuric.

423. All the baryta salts mentioned in the table are colourless, with the exception of the CHROMATE, which is of a *pale-yellow colour.*

424. *The following precautions must be attended to in examining for this group of acids*:—The first thing which claims attention is the state of the solution, viz., whether it be acid, alkaline, or neutral. When it is acid, ammonia must be added until it is slightly alkaline; should this cause a precipitate, filter off, and to the filtrate add chloride of barium; if no precipitate ensue on the addition of ammonia, add at once the baryta salt. Should the solution be alkaline, the alkalinity proceeding from one of the fixed alkalies, it would be better to neutralize with hydrochloric acid before adding the chloride of barium. Nitrate of baryta must be substituted for chloride of barium, and the precipitate produced be digested with nitric acid, when lead, silver, or suboxide of mercury is present. The precipitate must not be digested in undiluted acids, because chloride of barium and nitrate of baryta are insoluble in concentrated acids, and would therefore separate from the solution. When carbonic acid is present in the solution, it is better to get rid of it before adding the baryta salt; this is effected by adding to the solution hydrochloric acid, and boiling for a short time. When all the acid has been removed, add ammonia to neutralize the solution, and finally the baryta salt.

425. *Fourth Group.*—This group is merely a section of the last. The examination is commenced by adding to a portion of the original solution *chloride of calcium;* the precipitate

and hydrofluoric acid, as well as boracic acid, may be present, although ammonia causes no precipitate in the filtrate.

produced by this reagent, after being collected upon a filter and washed, must be digested with acetic acid. If complete solution ensue, HYDROFLUORIC ACID and OXALIC ACID are both (probably) absent. If the precipitate does not dissolve (or at least, not entirely), filter, and to the filtrate add one drop of sesquichloride of iron. If a precipitate be formed, it points out the probably presence of PHOSPHORIC ACID; should no precipitate be formed, that acid is probably absent. A special examination must be made in all cases for BORACIC ACID, OXALIC ACID, and HYDROFLUORIC ACID.

426. *The precautions to be attended to* are very similar to those given in the third group. The same plan must be pursued when the solution is acid or alkaline. Nitrate of lime must also be employed when silver, lead, or suboxide of mercury is present. When carbonic acid is present, it is better to get rid of it before adding the reagent. When much sulphuric acid is present, the solution ought to be diluted with water before adding the chloride of calcium, to prevent any sulphate of lime from precipitating. Arsenious and arsenic acids are precipitated by chloride of calcium from neutral solutions free from ammoniacal salts. When these acids are present, avoid the precipitation of their lime-salts by adding chloride of ammonium along with the chloride of calcium. Borate of lime and fluoride of calcium, like borate of baryta and fluoride of barium, are soluble in ammoniacal salts, from which solution they are not precipitated on the addition of ammonia: the non-formation, therefore, of a precipitate by chloride of calcium does not prove the absence of boracic or hydrofluoric acid, if ammoniacal salts are present.

427. *Fifth Group.—Nitrate of silver* precipitates, along with most of the acids previously noticed, the non-metallic elements, CHLORINE, BROMINE, IODINE, and the compound body CYANOGEN, from their combinations with hydrogen and the metals.

428. To a portion of the original solution must be added *nitrate of silver*. If a precipitate be produced, it must be digested with nitric acid, which will dissolve all the silver salts, with the exception of the CHLORIDE, CYANIDE, BROMIDE,

and IODIDE OF SILVER. WHEN THE SILVER PRECIPITATE does not completely dissolve in nitric acid, wash the insoluble portion so as to free it from all soluble silver salts, then add *ammonia*, and gently heat the mixture: the CHLORIDE, CYANIDE, and BROMIDE OF SILVER, being soluble in that reagent, will dissolve, whilst the IODIDE OF SILVER, being insoluble, will remain undissolved. When the silver precipitate does not completely dissolve in the ammonia, filter the mixture and add to the filtrate nitric acid in excess. If no precipitate is formed on the addition of the nitric acid, chlorine, bromine, and probably cyanogen, are absent. If a precipitate is formed, before proceeding to examine it further, test the original solution specially for cyanogen, either by the Prussian blue test (516) or by sulphide of ammonium (518); or, if protoxide of mercury has been discovered in testing for the bases, by the method described in par. 519.

429. WHEN CYANOGEN IS ABSENT, the silver precipitate, soluble in ammonia and insoluble in nitric acid, can only be due to bromine or chlorine, or both. The analyst must now test specially for bromine in the original solution (*see* par. 524). *When bromine is absent*, the silver precipitate, soluble in ammonia, and insoluble in nitric acid, can be due to the presence of chlorine only; *when bromine is present*, a special examination must be made for chlorine in the original solution, in the way described in par. 511.

430. WHEN CYANOGEN IS PRESENT, the silver precipitate, which has been thrown down from the ammoniacal solution by nitric acid, must, after it has been well washed by decantation, be transferred to a porcelain crucible, dried, and then ignited so as to decompose the cyanide of silver; and the residue, afterwards, must be boiled with dilute nitric acid. *If it all dissolves in the nitric acid*, bromine and chlorine are absent. *If the residue does not dissolve, or at least not entirely, in the nitric acid*, it points out the presence of bromine or chlorine, or both: fuse the insoluble portion with carbonate of soda and carbonate of potash, boil the fused mass with water and filter; examine a portion of the solution for bromine as

directed in par. 524; if it is found to be present the rest of the solution must be examined for chlorine, by the methods described in par. 511; but if *bromine is absent*, the silver precipitate insoluble in nitric acid could only be chloride of silver.

431. Some of the acids give with solutions of silver characteristic-coloured precipitates. Thus CHROMATE OF SILVER is *red;* SULPHIDE OF SILVER, *black;* ARSENIATE OF SILVER, *red;* SILICATE OF SILVER, *yellow* or *white;* ARSENITE, PHOSPHATE, and IODIDE OF SILVER, *yellow*. The rest of the acids give, with soluble silver salts, colourless precipitates.

432. *The following precautions must be attended to in analysing this group:*—The solution must be perfectly neutral *to test-paper:* an acid one is neutralized by adding ammonia slightly in excess, and then boiling the solution until all free alkali has been expelled. When a soluble sulphide or free hydrosulphuric acid is present, it is necessary, before testing with nitrate of silver, to remove the sulphur compound by adding nitric acid and warming the solution. When sulphate of the protoxide of iron is present, the silver salt will be reduced, metallic silver being precipitated. This may be obviated by converting the iron into peroxide: to effect this, boil the solution with a few drops of nitric acid.

433. The presence of the different acids, which the general reagents, *chloride of barium*, *chloride of calcium*, and *nitrate of silver*, have pointed out as existing in the solution, must be confirmed by the *special tests*.

434. *Sixth Group.*—A *special* examination must always be made for the acids contained in this group.

SPECIAL TESTS FOR THE INORGANIC ACIDS.

435. The special tests must be applied to the original solution; a separate portion must be taken for each acid.

436. CARBONIC ACID.—This acid is distinguished from the other gaseous acids by giving a precipitate with lime-water; the way for evolving the gas, when combined, and testing it,

TABLE VII.

BEHAVIOUR OF THE INORGANIC ACIDS WITH THE GENERAL REAGENTS.

ACIDS WHICH ARE GASEOUS AT THE COMMON TEMPERATURE AND PRESSURE.

Carbonic Acid, Hydrosulphuric Acid, Hydrocyanic Acid.

These acids are liberated from their combinations by the *stronger acids;* being set free, they immediately assume the gaseous state. The decomposition of their salts by acids is therefore attended with *effervescence.*

ACIDS WHICH ARE DECOMPOSED BY SULPHURETTED HYDROGEN.

Arsenious Acid, Arsenic Acid, Chromic Acid.

Arsenious and Arsenic Acid are converted by *sulphuretted hydrogen* into the corresponding Sulphur Acids, viz., Sulpharsenious and Sulpharsenic Acid, which are insoluble in the dilute mineral acids. Their presence or absence is therefore proved in testing for the bases—they in fact form a part of the fifth group.

Chromic Acid is converted, by the action of the *same reagent,* into a lower and basic Oxide (sesquioxide of Chromium), which belongs to the fourth group. The change of colour which attends this decomposition is very characteristic, viz., the conversion of a *yellow* or *orange-coloured* solution to a *green* one; the reduction is likewise attended with a separation of sulphur.

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY CHLORIDE OF BARIUM OR ANY SOLUBLE SALT OF BARYTA.

Carbonic Acid, Arsenious Acid, Arsenic Acid, Chromic Acid, Sulphuric Acid, Boracic Acid, Phosphoric Acid, Oxalic Acid, Hydrofluoric Acid, Silicic Acid.

The salts which these acids form with baryta are *all soluble* in hydrochloric acid, with the exception of *sulphate of baryta;* the solubility or insolubility of the baryta precipitate in acids is at once characteristic of the *presence* or *absence* of Sulphuric Acid.

TABLE VII.—*continued.*

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY CHLORIDE OF CALCIUM OR ANY SOLUBLE LIME SALT.

Boracic Acid, Phosphoric Acid, Oxalic Acid, Hydrofluoric Acid.

Phosphate of Lime and Borate of Lime are soluble in *acetic acid,* whilst Oxalate of Lime and Fluoride of Calcium are insoluble.

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY NITRATE OF SILVER.

Hydrosulphuric Acid, Arsenious Acid, Arsenic Acid, Chromic Acid, Boracic Acid, Phosphoric Acid, Oxalic Acid, Silicic Acid.

ACIDS WHICH ARE PRECIPITATED BOTH FROM A NEUTRAL AND ACID SOLUTION BY NITRATE OF SILVER.

Hydrochloric Acid, Hydrocyanic Acid, Hydrobromic Acid, Hydriodic Acid.

The silver salts of these acids are soluble in *ammonia,* with the exception of Iodide of Silver.

ACIDS WHICH ARE NOT PRECIPITATED BY ANY REAGENT.

Nitric Acid, Chloric Acid.

The salts of these acids *deflagrate* on ignited charcoal.

when liberated, with lime-water, is described in pars. 453 and 454.

437. SULPHIDE OF HYDROGEN.—This acid is distinguished from the other gaseous acids by giving, with soluble salts of silver and lead, black precipitates; the way for applying the test is described in par. 460. The sulphur in sulphides which are not decomposed by hydrochloric acid, but require for their decomposition nitric or nitro-hydrochloric acids, cannot be detected in this way: recourse must be had in these cases to the process described in par. 462.

438. HYDROCYANIC ACID.—This acid can be distinguished from all other acids by the tests described in pars. 516 and 518; if, however, protoxide of mercury has been discovered in testing for the bases, the process described in par. 519 must be employed.

439. ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID.—As these acids are discovered in testing for the bases, no experiments require to be made for their detection when testing for the acids.

440. SULPHURIC ACID.—The presence or absence of this acid is ascertained on testing a part of the solution with the general reagent, chloride of barium; no further test is needed to prove its absence or presence.

441. BORACIC ACID.—This acid can be detected, in most cases, by the method described in par. 478; but the most certain test is the one described in par. 479.

442. PHOSPHORIC ACID.—When the phosphates are soluble in ammoniacal solutions (and the student can decide this when he knows what bases are present), this acid can be detected by the method described in par. 484, but the most certain tests are 487 and 488, especially the last. The student must, however, remember that arsenic acid gives precipitates with these reagents, similar to those given by phosphoric acid. When arsenic acid is present, it must, on this account, be removed from the solution by sulphide of hydrogen, or be reduced to the state of arsenious acid, before testing for phosphoric acid.

443. Oxalic Acid.—This acid is detected by the method described at 495; but very minute quantities of it are more securely detected by boiling the substance with a solution of carbonate of soda, for some time; subsequently filtering, and acidifying the filtrate with acetic acid, and then adding to it a solution of sulphate of lime (494).

444. Hydrofluoric Acid.—Test for this acid, when silicic acid is absent, by the method described at 498; when silicic acid is present, by the one described at 500 or 501.

445. Silicic Acid.—To test for this acid, evaporate the solution to dryness with an acid, and proceed as directed at 505 or 506.

446. Hydrochloric Acid.—When hydrocyanic acid and hydrobromic acid are absent, the presence of this acid is proved by the insolubility of the silver precipitate in nitric acid, and by its solubility in ammonia; when hydrocyanic acid is present, and hydrobromic acid absent, its presence is proved, if, after igniting the silver precipitate, which is insoluble in nitric acid, but soluble in ammonia, a whitish residue remains, which is insoluble in nitric acid. When hydrobromic acid is present, no matter whether hydrocyanic acid is present or absent, the presence of hydrochloric acid can only be ascertained by the test described at 511.

447. Hydrobromic Acid.—When hydrocyanic acid or a cyanide is present, examine for bromine according to the method given in par. 430; when cyanogen compounds are absent examine for bromine according to par. 524.

448. Hydriodic Acid.—Iodine is best discovered by the test described at 535.

449. Nitric Acid.—The tests described at 544, 545, 550, and 551, may be employed; but for the detection of the acid in waters the test described at 547 is the best.

450. Chloric Acid.—The presence or absence of this acid is proved by the tests described at 555 and 556.

Carbonic Acid (CO_2).

451. This acid exists at the common temperature and pres-

sure as a colourless, inodorous, and non-inflammable gas. Being heavier than the atmosphere in the proportion of 1·5 to 1, it can be decanted from one vessel to another like a liquid. It reddens blue litmus paper previously moistened with water, which after a time returns to its original colour, owing to the acid having volatilized. It is soluble in cold water, but when the solution is heated the gas escapes.

452. The neutral alkaline carbonates are the only *neutral* salts of this acid which are soluble in pure water. The carbonates are decomposed by all free acids soluble in water (hydrocyanic and hydrosulphuric acids excepted), with evolution of carbonic acid.

453. *To detect* carbonic acid, add to the solution or solid substance under examination *hydrochloric acid;* and warm the solution, if sufficient gas for detection cannot be procured without. Should any gas be evolved, allow it to accumulate by placing the thumb on the mouth of the test-tube, and afterwards decant it (taking care not to allow any of the liquid to pass over along with it) into another test-tube half filled with *lime-water*. A white precipitate of CARBONATE OF LIME will be produced, if carbonic acid is present.

454. When the solution under examination contains only a minute quantity of a carbonate, it is sometimes a matter of difficulty, especially to young students, to decant the carbonic acid into the test-tube half filled with lime-water; this is especially the case if phosphate of soda is also present in the solution, as carbonic acid is very soluble in a solution of that salt. In such cases it would be better first to precipitate the carbonic acid in conjunction with lime or baryta, by adding to the solution under examination a solution of chloride of calcium or chloride of barium, collecting the precipitate produced upon a filter and after all the fluid has filtered off to transfer the precipitate again to the test-tube. Moisten with water, then add hydrochloric acid, and if any effervescence takes place to collect the gas in lime-water in the manner just described (453).

455. *Chloride of calcium* and *chloride of barium* produce in

solutions of the neutral alkaline carbonates an *immediate* precipitate of CARBONATE OF LIME or of CARBONATE OF BARYTA; but these chlorides in dilute solutions of the bicarbonates form precipitates only after *ebullition;* in solutions of free carbonic acid these reagents produce no precipitates.

456. Many of the insoluble carbonates dissolve in water containing free carbonic acid—from which solutions they are precipitated on boiling, the free acid being expelled. It is in this state that most of the lime and magnesia in spring and river water exists. The incrustations which are formed in the vessels in which such waters are boiled are due to the precipitation of these carbonates occasioned by the removal of the free carbonic acid. Carbonic acid is best detected in waters by adding to them *lime-water;* by this means not only is the CARBONATE OF LIME which is formed precipitated, but also that which pre-existed in the solution. This process is employed on a large scale for softening hard waters (waters impregnated with earthy matter).

457. All the carbonates, with the exception of those of the alkalies, lose their acid upon ignition, the metal being left either in an oxidized or uncombined state, according to its greater or less affinity for oxygen. The alkaline carbonates and bicarbonates affect test-paper in the manner of a free alkali.

458. *The following precautions must be attended to in testing for this acid:*—When the substance is in the solid state, it should be reduced to fine powder; and a little water should be added prior to the acid, to displace the air in its pores, otherwise an apparent effervescence will ensue from the expulsion of air. In the case of alkaline carbonates, the decomposing acid must be added until the solution reddens blue litmus paper—that is, until the acid is in *excess;* otherwise, the carbonic acid set free may combine with some of the undecomposed carbonate, forming with it a bicarbonate, no effervescence consequently taking place. No decomposition takes place on the addition of strong nitric acid to carbonate of baryta, especially the native carbonate, because nitrate of baryta is insoluble in the strong acid. Water must therefore

be added, as well as the acid, for the decomposition to be effected in this and many other cases.

HYDROSULPHURIC ACID (*Sulphuretted Hydrogen* HS).*

459. This acid exists at the common temperature and pressure as a colourless inflammable gas possessing a highly offensive odour resembling that of rotten eggs. It burns with a blue flame, the products of combustion being sulphurous acid and water. It is soluble in water, three volumes of which dissolve one volume of the gas; this solution reddens litmus paper. On exposing the gas in a state of solution to the air, it is decomposed, water being formed, and sulphur in a highly divided state being separated.

460. Most metallic sulphides dissolve with decomposition in *hydrochloric acid*, in which case SULPHURETTED HYDROGEN is evolved, which from its characteristic smell is easily recognised. When the quantity is so minute that the smell fails to afford a sufficient proof, it may be detected by holding a piece of paper moistened with a solution of any soluble SALT OF LEAD over the mouth of the test-tube, as a brown or black coating of SULPHIDE OF LEAD will be formed upon the paper.

461. When sulphides are dissolved in *nitric* or *nitro-hydrochloric acid*, SULPHURIC ACID is formed along with a separation of sulphur, which may be recognised by its colour, and also its behaviour upon ignition. In the case of sulphides, therefore, which, from their insolubility in hydrochloric acid, must be dissolved in nitric or nitro-hydrochloric acids, the sulphur is converted into *sulphuric acid*, and not given off as sulphuretted hydrogen.

462. To ascertain whether the sulphur existed in an unoxidized state, when nitric or nitro-hydrochloric acid has been employed as the solvent of the substance under examination, a small portion of the *original* substance, in fine powder, must be fused with a little solid hydrate of potash or soda, in a platinum spoon, by means of the blowpipe flame. The fused mass must then be dissolved in a little water and filtered; a bright strip of silver (or polished coin) is put into the solution,

and the fluid warmed. If a sulphide were present, a brownish-black film of sulphide of silver would form upon the metal. This film may be removed afterwards by rubbing the metal with leather and quicklime.

463. When the sulphides of the heavy metals are heated in contact with air, sulphurous acid is evolved: the metal being left in some cases uncombined, and in others as an oxide. The sulphides of the alkalies and alkaline earths are converted by this process into sulphates. As the student is made familiar in passing through the basic groups, with the properties of the various sulphides, their solubility or insolubility in water, the alkalies, and the various acids, their colour, &c., it is unnecessary to notice them here.

CHROMIC ACID (CrO_3).

464. Chromic acid is a solid coloured acid occurring in the form of beautiful crimson needles, which deliquesce rapidly when exposed to the air, the solution possessing a deep red-brown tint. This acid is decomposed, upon ignition, into sesquioxide of chromium and oxygen. All its salts are coloured; the neutral chromates possessing a yellow, and the acid or bichromates a red colour. Most of the salts are insoluble in water; they are nearly all soluble in nitric acid.

465. Chromic acid, whether in its free or combined state, is reduced by *hydrosulphuric acid* to the state of SESQUIOXIDE OF CHROMIUM; water and some oxide of sulphur is formed in this decomposition, along with a separation of sulphur. The change of colour which attends this decomposition, viz. the conversion of a yellow or red coloured solution to a green one, is so characteristic that it cannot be mistaken.

466. "Chromic acid may also be reduced to sesquioxide of chromium by means of many other substances, and more particularly by *sulphurous acid*, or by heating with *hydrochloric acid*, especially upon the addition of alcohol (in which case chloride of ethyl and aldehyde are evolved); also by *metallic*

zinc, or by heating with *tartaric acid*, *oxalic acid*, &c. All these reactions are clearly characterised by the change of the red or yellow colour of the solution to the green tint of the salt of the sesquioxide of chromium.

467. "If a very dilute acid solution of *peroxide of hydrogen** is covered with a layer of ether and a fluid containing chromic acid is added, the solution of peroxide of hydrogen acquires a fine blue colour. By inverting the test-tube closed with the thumb, repeatedly, without much shaking, the solution becomes colourless, whilst the ether acquires a blue colour. The latter reaction is particularly characteristic. One part of chromate of potash in 40,000 parts of water suffices to produce it distinctly (*Storer*); presence of vanadic acid materially impairs the delicacy of the test (*Werther*). The blue coloration is in all probability caused, not by perchromic acid (the existence of which is altogether doubtful), but by a combination of chromic acid with peroxide of hydrogen. After some time reduction of the chromic acid to sesquioxide of chromium takes place, and at the same time decoloration of the ether."—*Fresenius.*

468. Alkaline chromates may be prepared from insoluble chromates by fusing the latter in conjunction with alkaline carbonates.

469. When testing for the bases, we always find the chromic acid as sesquioxide of chromium, since hydrosulphuric acid reduces it to that state.

SULPHURIC ACID (*Oil of Vitriol*) (HO, SO_3).

470. Anhydrous sulphuric acid (SO_3) is a white feathery crystalline mass, which, when exposed to the air, emits dense

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* Solution of peroxide of hydrogen may be easily prepared by triturating a fragment of peroxide of barium (about the size of a pea) with some water, and then adding a little dilute hydrochloric acid. The solution keeps a long time without suffering decomposition. In default of peroxide of barium, impure peroxide of sodium may be used instead, which is obtained by heating a fragment of sodium in a small porcelain dish until it takes fire, and letting it burn.

white fumes. It is destitute of acid properties until it has combined with water and passed into the hydrated state. The hydrated acid is a heavy colourless, oily fluid, which possesses a strong affinity for water, producing when mixed with it, a great degree of heat. Its affinity for water is so great, that it decomposes organic substances when placed in contact with them, removing their hydrogen and oxygen, whilst the carbon is left behind as a black coaly mass, a portion of which dissolves in the acid and communicates to it a brown tint. If heat is applied, the carbon is oxidized at the expense of the sulphuric acid, carbonic acid and sulphurous acid being formed; these facts may be illustrated by pouring some strong sulphuric acid upon white sugar. Sulphuric acid, at temperatures below its boiling-point (572° F.), displaces all other acids from their combinations with bases, but above that temperature it is itself displaced by the non-volatile acids.

471. Most of the sulphates, with the exception of the sulphates of baryta, strontia, and lead, are soluble in water. The alkaline sulphates and the three just named are the only salts of this acid which are not decomposed on simple ignition.

472. Sulphates in dilute solutions containing organic matter are gradually converted into sulphides. Water containing a sulphate may therefore, after it has been kept a long time in a bottle or any closed vessel, be found to contain sulphuretted hydrogen, although originally it was perfectly free from that gas.

473. Sulphate of baryta, *from its insolubility in acids*, is at once distinguished from all the other baryta salts; any *soluble salt of baryta* is therefore the best and most delicate test for SULPHURIC ACID.

474. Insoluble sulphates are completely decomposed by fusion with *alkaline carbonates*, an ALKALINE SULPHATE being produced along with a CARBONATE or an OXIDE of the METAL.

475. When a sulphate, mixed with *charcoal* and *carbonate of soda*, is fused upon a charcoal support by the inner blowpipe

flame, sulphide of sodium is produced. If the fused mass, moistened with water, be placed upon a piece of silver, a brown stain of sulphide of silver will be formed.

476. "To detect free sulphuric acid in presence of a sulphate, the fluid under examination is mixed with a very little cane-sugar, and the mixture evaporated to dryness in a porcelain dish at 212° Fahr. If free sulphuric acid was present a black residue remains, or, in the case of most minute quantities, a blackish-green residue. Other acids do not decompose cane-sugar in this way."

BORACIC ACID (BO_3).

477. This acid is best obtained by adding to a boiling concentrated solution of biborate of soda (borax) strong sulphuric acid, until the liquor becomes sour to the taste; on cooling, the greater part of the boracic acid separates from the solution in the form of colourless crystalline scales, containing water. When ignited, they fuse to an anhydrous glassy mass, which, on exposure to the air, absorbs water, swells, and becomes opaque. This acid, in the anhydrous state, is a colourless fixed glass, fusible at a red heat; the hydrate ($2BO_3, 3HO$) is a porous white mass; in the crystalline state ($2BO_3, 3HO+3$ aq.) it presents small scaly laminæ. The hydrated acid is much more soluble in hot than cold water. When an alcoholic or an aqueous solution of this acid is evaporated, a portion of the acid volatilizes with the vapours of the solvent, but alone it is perfectly fixed at a red heat. One peculiar property which this acid possesses is that of affecting turmeric paper in the manner of a free alkali; it acts, however, on blue litmus paper like other acids. All the borates, with the exception of the alkaline ones, are almost totally insoluble in pure water; they dissolve readily in acids, and in water containing ammoniacal salts. They are not decomposed upon ignition; they are colourless, and all of them, *even the acid salts*, manifest an alkaline reaction.

478. An alcoholic solution of boracic acid burns with a

green-coloured flame, which becomes more distinct upon stirring the mixture. To detect a borate, add to the substance under examination *strong sulphuric acid* and *alcohol* or *wood naphtha;* ignite the mixture subsequently. If a borate be present, the borders of the flame will appear *green*, which becomes more distinct upon stirring, and the delicacy is further increased by repeatedly extinguishing and rekindling the flame. The only substance which at all interferes with this test is copper, the salts of which impart the same colour to the flame. This metal, if present, must therefore be got rid of by sulphuretted hydrogen, before testing for boracic acid.

479. A solution of one part of borax in one thousand parts of water, *very slightly* acidified with hydrochloric acid, imparts to turmeric paper, after drying, a distinctly red tint (*H. Rose*). This method may therefore be employed in place of the usual method for the detection of boracic acid. The slip of paper ought only to be dipped *half* into the fluid, and it ought to be dried on a piece of glass at a temperature of 212° F.

PHOSPHORIC ACID ($3HO, PO_5$).

480. Anhydrous phosphoric acid (PO_5) appears under the form of white flakes, which rapidly absorb moisture from the atmosphere. It has a great affinity for water, with which it combines in three different proportions, forming three distinct acids, which have the following constitution—

Tribasic phosphoric acid ($3\ HO, PO_5$).
Bibasic phosphoric acid ($2\ HO, PO_5$).
Monobasic phosphoric acid (HO, PO_5).

481. Each of these acids forms, with bases, a distinct class of salts.

482. The tribasic acid, which is the most important, is the only one treated of in this work. It appears in the form of colourless crystals, which deliquesce rapidly in the air. When strongly heated in an open platinum vessel, it volatilizes without a residue.

483. The neutral phosphates, with the exception of the alkaline ones, are nearly all insoluble in water. The action of heat converts the tribasic phosphates into bibasic or monobasic salts, according to the number of atoms of basic water expelled.

484. *Sulphate of magnesia*, or *any soluble magnesian salt*, produces in aqueous solutions of the phosphates, if concentrated, a white precipitate of PHOSPHATE OF MAGNESIA ($2MgO,HO,PO_5$). A salt much more insoluble in water, is produced by adding *chloride of ammonium*, *ammonia*, and then the *magnesian salt;* in this way PHOSPHATE OF MAGNESIA AND AMMONIA ($2MgO,NH_4O,PO_5$) is precipitated, which is slightly soluble in pure water, but almost insoluble in water containing ammonia. In dilute solutions it only appears *after much agitation and the lapse of some time;* agitation promotes its formation in all cases. This test can only be applied when the phosphates are soluble in ammoniacal solutions.

485. *Acetate of lead* produces a white precipitate of PHOSPHATE OF LEAD ($3PbO, PO_5$), which is soluble in nitric acid. If this precipitate, after being dried, is heated in the outer flame of the blowpipe, it becomes distinctly crystalline on cooling. This test is very characteristic, not only on account of the crystalline structure of the bead, but also from the circumstance that the phosphate of lead is the only salt of that metal which is not reduced to the metallic state when heated in the inner blowpipe flame. It is evident that, to render this test of any value, the phosphate of lead must be freed thoroughly, by washing, from all acetate of lead.

486. *Nitrate of silver* throws down, both from solutions of phosphates containing one or two atoms of fixed base, as well as from phosphates containing three atoms of fixed base, a light yellow precipitate of phosphate of silver ($3 AgO, PO_5$), which is readily soluble in nitric acid and in ammonia. If the solution contained a phosphate containing three atoms of fixed base, the fluid in which the precipitate is suspended will manifest a neutral reaction, whilst the reaction will be acid if the

solution contained a phosphate containing one or two atoms of fixed base. The acid reaction is occasioned by the nitric acid receiving, for the three equivalents of oxide of silver which it yields to the phosphoric acid, only 2 or 1 eq. of fixed base, and 1 or 2 eq. of water; and as the latter does not neutralize the acid properties of the nitric acid, the solution becomes acid. Monobasic and bibasic phosphate of silver is white; consequently, a tribasic phosphate containing 1 or 2 eq. of fixed base, yields, after ignition, a white precipitate with nitrate of silver (AgO, PO_5, or $2\ AgO, PO_5$).

487. "If to a solution containing phosphoric acid and the *least possible excess* of hydrochloric or nitric acid a tolerably large amount of acetate of soda is added, and then a drop of *sesquichloride of iron*, a yellowish-white flocculent-gelatinous precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON is formed. An excess of sesquichloride of iron must be avoided, as acetate of sesquioxide of iron (of red colour) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths; but it can be held to be decisive only if no arsenic acid is present, as this acid gives the same reaction. To effect the complete separation of the phosphoric acid from the alkaline earths, a sufficient quantity of sesquioxide of iron is added to impart a reddish colour to the solution, which is then boiled (whereby the whole of the sesquioxide of iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of sesquioxide of iron, boil the hydrochloric acid solution with sulphite of soda, until the sesquichloride is reduced to protochloride, which reduction is indicated by the decoloration of the solution; add carbonate of soda, until the fluid is nearly neutral; then acetate of soda, and finally, one drop of sesquichloride of iron. The reason for this proceeding is, that acetate of protoxide of iron does not dissolve phosphate of sesquioxide of iron.

488. "If some *molybdate of ammonia* is mixed in a test-tube

with hydrochloric or nitric acid, in sufficient quantity to redissolve the precipitate which forms at first, and a little of a very dilute fluid containing phosphoric acid is then added, and the mixture slightly warmed, the fluid acquires an intensely yellow colour, and after some time a yellow precipitate separates, which is insoluble in hydrochloric acid. The exact composition of this precipitate is not yet ascertained; we only know that it contains MOLYBDIC ACID, AMMONIA, and a little PHOSPHORIC ACID. Application of heat greatly promotes the reaction. This reaction is so delicate that the phosphoric acid may be detected by its means in almost all salts and most minerals containing it. As the yellow compound is decomposed by free phosphoric acid, an excess of the fluid containing the phosphoric acid must be carefully avoided. The yellow precipitate may, when it has subsided, be perceived even in dark-coloured fluids.

489. "In phosphate of alumina the phosphoric acid may be detected also by one of the two following methods:

490. "Add carbonate of soda to the hydrochloric acid solution until the free acid is nearly neutralized; mix with carbonate of baryta in excess; add solution of soda or potash, and boil. This process gives the alumina in solution, the phosphoric acid in a precipitate of phosphate of baryta. Dissolve this precipitate in hydrochloric acid, decompose by sulphuric acid, filter, and test the filtrate with sulphate of magnesia, with addition of chloride of ammonium and ammonia.

491. "Mix the hydrochloric acid solution with tartaric acid; add ammonia in excess; and finally, to the clear solution, chloride of ammonium and sulphate of magnesia. If a precipitate forms only after some time, this cannot be considered a safe indication of the presence of phosphoric acid, as under the circumstances named, a precipitate of tartrate of magnesia, resembling the phosphate of magnesia and ammonia, may form in a solution of the proper degree of concentration, though no phosphoric acid is present. The precipitate must therefore be tested for phosphoric acid, which is done by dissolving it in nitric acid, evaporating the solution, with addition of some pure nitrate of potash or soda, to dryness, igniting the residue,

then heating with hydrochloric acid, filtering the solution, and mixing the filtrate with ammonia in excess. The formation of a crystalline precipitate of phosphate of magnesia and ammonia confirms the presence of phosphoric acid."—*Fresenius.*

OXALIC ACID (HO, C_2O_3, or $HO, \bar{O}$).

492. Oxalic acid crystallizes from its aqueous solutions in four-sided prisms. These crystals contain three atoms of water, of which one is essential ($HO, C_2O_3 + 2$ aq.). When warmed, the 2 atoms of non-essential water (water of crystallization) are given off, and the hydrate of oxalic acid remains as a white powder, which melts at 350°, and, when further heated, sublimes—a portion, however, being decomposed. It is very soluble in water, and highly poisonous. It is usual to place it in the list of organic acids; but since its salts upon ignition leave no carbonaceous residue, it has been included in the list of inorganic acids.

493. All the oxalates are decomposed at a red heat, the oxalic acid being resolved into carbonic acid and carbonic oxide. If the base with which the acid is combined be an alkali or an alkaline earth, it is left as a carbonate; the other bases are left either in an oxidized or metallic state, according to their greater or less affinity for oxygen.

494. *Lime-water* and all the soluble *salts of lime* produce in solutions of oxalic acid and the oxalates, even if highly diluted, a white precipitate of OXALATE OF LIME, which is insoluble in acetic acid.

495. When *concentrated sulphuric acid* is added to dry oxalic acid or an oxalate, it withdraws the constitutional water in the one case and the base in the other from the anhydrous acid (C_2O_3), which, being incapable of existing alone, splits up into CARBONIC ACID and CARBONIC OXIDE. The two gases escape with effervescence; and if a light be applied as they issue from the mouth of the tube, the carbonic oxide will burn with a blue flame.

496. If oxalic acid or an oxalate is mixed with some finely powdered *binoxide of manganese* (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence ensues, caused by the escaping carbonic acid ($MnO_2+HO, C_2O_2+HO, SO_3 = MnO, SO_3+2 HO+2 CO_2$).

HYDROFLUORIC ACID (HF).

497. This acid is best obtained by the action of concentrated sulphuric acid on fluoride of calcium (fluor spar). The powdered mineral is gently heated with the acid in a retort of lead, and the acid condensed in a receiver of the same metal. It is obtained in the form of a very volatile liquid, strongly acid and corrosive, fuming in the air. It burns the skin like red-hot iron, causing a sore which is not easily healed. It is distinguished from all other acids by dissolving insoluble silicic acid and the silicates which are insoluble in the other acids; on this account it cannot be prepared or kept in glass vessels.

498. "If a finely pulverized fluoride, no matter whether soluble or insoluble, is heated in a platinum crucible with concentrated sulphuric acid, the crucible covered with the convex face of a watch-glass, coated on that side with bees'-wax, which has been removed again in some places by tracing lines in it with some pointed instrument,* the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found etched into the glass. If the quantity of hydrofluoric acid disengaged by the sulphuric acid is very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This reappearance of the etched lines

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* The coating with the wax may be readily effected by heating the glass cautiously, putting a bit of wax upon the convex face, and spreading the fused mass equally over it. The instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers best. The removal of the wax coating is effected by heating the glass gently and wiping the wax off with a cloth.

is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess."—*Fresenius.* This method cannot be adopted if the substance containing the fluorine is not decomposed by sulphuric acid, or if *silicic* acid is present; the silicic acid must be got rid of, in the way to be described, before we can discover fluorine.

499. If nascent hydrofluoric acid meet with silicic acid, the two compounds are mutually decomposed, FLUORIDE OF SILICON (SiF_3) and water being formed. Should the compound examined contain therefore silicic acid as well as fluorine, fluoride of silicon, and not hydrofluoric acid, will be disengaged by the sulphuric acid. Fluoride of silicon in the pure state is a colourless gas, which has a suffocating acid smell, and which emits fumes in contact with the air. It is largely soluble in water, but is thereby partially decomposed; silicic acid is deposited in the gelatinous state, and a combination of fluoride of silicon and of hydrofluoric acid is dissolved (hydrofluosilicic acid HF, SiF_3). Fluoride of silicon does not attack glass. The glass, when damp, becomes covered with a very adhesive coating of silica which impairs the transparency of the glass, owing to the decomposition of the fluoride of silicon. It is necessary to notice the action of bases upon hydrofluosilicic acid, as the method next to be described cannot be well understood without this knowledge. Hydrofluosilicic acid combines with the basic metallic oxides, and forms with them a class of salts called silicofluorides. In order, however, to obtain these silicofluorides, it is necessary to have the acid in excess, or at any rate to use as much of it as is necessary to saturate the acid base; for when an excess of base is employed, the hydrofluosilicic acid is decomposed, the silicon separates in the form of silicic acid, and a fluoride remains in solution.

500. The method for detecting fluorine in the presence of silicic acid is founded upon the fact just stated—that when a fluoride, combined or mixed with silica, is heated with sulphuric acid, the fluorine and silicon are evolved in combination as fluoride of silicon. This method is applicable to all silicated

fluorides which are *decomposable by sulphuric acid.* Boil the substance under examination with concentrated sulphuric acid in a flask, retort, or test tube, to which is attached a bent tube; conduct the gases evolved into a solution of ammonia; heat, filter, evaporate in a platinum crucible to dryness, and examine the residue by the method described in 435. If the substance under examination contains only a slight trace of fluorine and no other volatile acid, it is better to add a very little marble to the substance, so as to ensure a continuous slight evolution of gas. When the sulphuric acid boils, all the fluoride of silicon is given off.

501. " Compounds not decomposable by sulphuric acid must first be fused with four parts of carbonate of soda and potash. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel, hydrochloric acid added to feebly acid reaction, and the fluid let stand until the carbonic acid has escaped. It is then super-saturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 435."—*H. Rose.*

502. If a fluoride mixed with bisulphate of potash is heated in a test-tube, hydrofluoric acid is disengaged, which is easily detected by the etching of the glass. Consult also pars. 675 and 667, 9*th b.*

SILICIC ACID (*Silica* SiO_3).

503. The anhydrous acid is met with in two states—crystalline and uncrystalline, or amorphous. In both these states it is insoluble in water and all acids with the exception of hydrofluoric acid. The hydrated acid is slightly soluble in water and the ordinary acids; it is rendered anhydrous and insoluble by heat. Its aqueous solution does not redden blue litmus paper, or possess any taste; the presence of the acid can only be detected with certainty by evaporating the solution

to dryness, and thus obtaining it in its insoluble form, as a gritty, whitish powder, which remains undissolved when the dry mass is treated with water or dilute acids. Its presence should be further confirmed by testing the gritty powder with carbonate of soda before the blowpipe flame, as directed at 508. The amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of the fixed caustic and carbonated alkalies, but the crystalline acid is insoluble in these reagents.

The crystallized acid is, as has been stated, dissolved by hydrofluoric acid; it is also rendered soluble by fusing it with the fixed carbonated alkalies, a basic silicate being obtained, which is soluble in water, and from which acids separate it in the hydrated state. If there is sufficient water to dissolve it, when it is thus separated from basic bodies, it does not precipitate; but if there be not sufficient water present, then a portion of the acid, varying with the amount of water, precipitates, owing to its being a solid body. Silicic acid, when quite pure, is a colourless or white powder, which is more or less gritty; it is infusible and unalterable in the hottest blowpipe flame, but fuses in the flame of the oxyhydrogen blowpipe.

504. The alkaline silicates are the only salts of this acid which are soluble in water. Some of the silicates insoluble in water are dissolved with decomposition by hydrochloric or nitric acids; some of them, that are not even affected by these acids when the mixture is boiled, are decomposed by concentrated sulphuric acid. The silicates which are not acted upon by any acids but hydrofluoric acid, are decomposed by fusion with the alkaline carbonates, and also with hydrate of baryta.

505. The solution of the alkaline silicates is decomposed by all acids, even by carbonic acid. If there is not sufficient water present to dissolve the silicic acid when the silicate is decomposed, a part of it precipitates as hydrate, in the form of a gelatinous mass. If a solution of an alkaline silicate be evaporated to dryness along with a slight excess of hydrochloric or nitric acid, and if the dry mass be ignited for some

little time and then treated with dilute hydrochloric or nitric acid, the other substances dissolve, whilst the whole of the silicic acid remains undissolved as a gritty powder of a whitish colour. On adding chloride of ammonium to a concentrated solution of an alkaline silicate, a gelatinous precipitate* takes place.

506. The silicates decomposable by hydrochloric or nitric acid ought to be reduced to the finest powder, before acting upon them with either of the acids; when the acid is added, the silicate must be digested in the acid at or near the boiling point for some time. To effect the complete separation of the silica from the bases and other acids, the acid mixture is evaporated to dryness, the silicate is thus completely decomposed, but the heat must be continued until there is no longer the least trace of acid fumes, in order to render the whole of the silicic acid insoluble; the dry mass is then boiled with dilute hydrochloric acid; the solution containing the bases and other acids is filtered off from the insoluble silica, which is examined according to 508.

507. The decomposition of the silicates which are not decomposable by hydrochloric or nitric acid, is best effected by fusing them with four times their weight of a mixture of carbonate of soda and carbonate of potash. The silicate must be reduced to the finest powder, and then intimately mixed with the alkaline carbonates, also in a state of fine powder; the mixture is then to be heated, by means of a gas lamp or Berzelius spirit-lamp, in a platinum crucible, until the mixture is in a state of fusion. The crucible is then allowed to cool; and when cold or nearly so, and still containing the fused mass, it is put into an evaporating dish containing dilute hydrochloric acid. When the fused mass is detached from the crucible, remove the crucible and evaporate the mixture to dryness, and ignite just in the same way as the solution in 506 is directed to be treated. The fixed alkalies cannot of course be sought

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* Is this precipitate, which is always looked upon as hydrated silicic acid, a silicate of ammonia, corresponding to the titanate of ammonia discovered by Rose?

for in that portion which has been fused with the alkaline carbonate; to ascertain whether they are present, another portion of the silicate must be fused with hydrate of baryta. For this purpose "mix one part of the very finely pulverised substance with four parts of hydrate of baryta; expose the mixture for half an hour, in a platinum crucible, to the strongest possible heat of a good Berzelius spirit-lamp or to a gas lamp, and treat the fused or agglutinated mass with hydrochloric acid and water until it is dissolved. Precipitate the baryta and all the bases in the silicate, with the exception of magnesia and the alkalies, with ammonia and carbonate of ammonia; filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, ignite;" then test for potash and soda in the usual way.

508. When silicic acid is fused with *carbonate of soda* before the blowpipe, a transparent colourless bead is formed, while carbonic acid is expelled. A small quantity of soda ought only to be employed, as an opaque bead is produced when it is added in excess.

HYDROCHLORIC ACID (*Muriatic Acid*, HCl).

509. This acid is a transparent and colourless gas, of a pungent, acid, suffocating smell, and fuming strongly with moist air. It is absorbed in large proportions by water, forming the common liquid hydrochloric acid, which is a mere solution of the gas in water.

510. When a chloride is heated with *peroxide of manganese* (MnO_2) and *sulphuric acid*, chlorine gas is evolved, which may be recognised by its ODOUR and GREENISH-YELLOW COLOUR.

511. When a chloride is heated with *chromate of potash* and *concentrated sulphuric acid*, a brown gas is disengaged, which condenses into a blood-red liquid, CHROMATE OF CHLORIDE OF CHROMIUM ($CrCl_3$, 2 CrO_3). On the addition of ammonia in

excess, the colour changes to a yellow, owing to the formation of neutral chromate of ammonia; upon the addition of an acid, the yellow changes to a reddish-yellow colour, owing to the formation of an acid chromate.

512. If in a bead of phosphate of soda and ammonia on a platinum wire, *oxide of copper* be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLOURED flame, inclining to PURPLE, will be seen encircling it so long as chlorine is present. (*Berzelius.*)

HYDROCYANIC ACID (*Prussic Acid*, H, C_2N, or HCy).

513. This acid is the hydrogen compound of the radical cyanogen (C_2N), a compound composed of carbon and nitrogen.

514. In its anhydrous state hydrocyanic acid is a colourless, volatile, inflammable liquid, possessing a strong odour resembling oil of bitter almonds. Water dissolves it in all proportions; both in its concentrated and diluted state it speedily undergoes decomposition when exposed to the light. Being exceedingly poisonous, it requires to be used with care.

515. The cyanogen compounds of the metals of the alkalies and alkaline earths are soluble in water; their solutions possess an alkaline reaction, and are decomposed, with the liberation of hydrocyanic acid, by the weakest acid.

516. If to a solution of free hydrocyanic acid or an alkaline cyanide, *potash* and a mixed solution of a *per-* and *proto-salt of iron* be added, a greenish-blue precipitate will be produced, which consists of a mixture of Prussian blue ($Fe_4\ Cfy_3$), and the hydrates of per- and protoxide of iron; on the addition of hydrochloric acid, the oxides of iron dissolve, but the *Prussian blue* remains undissolved. If only a very minute quantity of hydrocyanic acid is present, the fluid simply appears green

after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it.

517. "If to a solution of hydrocyanic acid potash is added in excess, and then finely pulverised *peroxide of mercury*, the latter dissolves as readily as it would in free hydrocyanic acid. Since peroxide of mercury is soluble in alkaline fluids *only in presence of hydrocyanic acid*, this reaction may be looked upon as a positive test for that acid."—*Fresenius.*

518. When free hydrocyanic acid is added to sulphide of ammonium containing an excess of sulphur, the acid seizes upon some of the ammonia and sulphur, forming with them SULPHOCYANIDE OF AMMONIUM (NH_4, CyS_2), which possesses, in common with all the other soluble sulphocyanides, the property of producing with persalts of iron a *deep blood-red colour.* This test may be applied in qualitative analysis in the following way:—Add a few drops of *yellow* sulphide of ammonium to the liquid supposed to contain the hydrocyanic acid; evaporate at a *gentle heat* (not above 212° F.), until the excess of sulphide of ammonium has completely volatilized, which is ascertained by the smell; then test the solution with a drop or two of sesquichloride of iron. This test is exceedingly delicate. "If an acetate is present, the reaction takes place only upon addition of hydrochloric acid." (*Fresenius.*)

519. "Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. To detect cyanogen in that compound, the solution is mixed with sulphide of hydrogen; sulphide of mercury precipitates, the solution then contains free hydrocyanic acid." Examine the solution, after the precipitation of the mercury, for hydrocyanic acid, either by the method described in 516 or 518.

HYDROBROMIC ACID (HBr).

520. Hydrobromic acid is a gas which resembles very closely in its properties hydrochloric acid gas. It emits in the air white fumes, which are denser than those produced by hydro-

chloric acid gas. It is decomposed by chlorine, bromine being set free, and hydrochloric acid formed; the liberated bromine appears under the form of reddish vapours, or if in more considerable proportions, it condenses into drops of a similar colour. Hydrobromic acid gas is extremely soluble in water; the solution is colourless, and, both in the concentrated or in the dilute state, it very much resembles concentrated or dilute hydrochloric acid. When, however, hydrobromic acid gas contains any free bromine, which it dissolves in large quantities, the liquid acid has a dark reddish colour.

521. Bromine is soluble in water, but it is much more soluble in alcohol, ether, chloroform, and bisulphide of carbon; the solutions are reddish yellow. Free bromine, especially in its vaporous state, turns moistened starch yellow, bromide of starch which is of a yellow colour being formed; the yellow colour is not always instantaneous.

522. Hydrobromic acid and the bromides, with the exception of bromide of silver and bromide of mercury are decomposed by *nitric acid*, on the application of heat, the hydrogen of the metal being oxidized and the bromine liberated; if the bromide operated upon is in the solid state or as a concentrated solution, the bromine vaporizes; but if the bromide is in a state of solution and not very concentrated the liberated bromine dissolves in the liquid, colouring it yellow or yellowish-red. In the cold, nitric acid, even the fuming red acid, does not liberate bromine from moderately dilute solutions of the bromides, nor is it liberated by a solution of hyponitric acid in sulphuric acid, or by hydrochloric acid and nitrite of potash.

523. "*Chlorine*, in the *gaseous state* or in *solution*, immediately liberates bromine in the solutions of its compounds; the fluid assuming a yellowish-red tint if the quantity of bromine present is not too minute. A large excess of chlorine must be avoided, since this will cause formation of chloride of bromine, which will destroy the colour wholly or nearly so. This reaction is made much more delicate by addition of a fluid which dissolves bromine and does not mix with water, as sulphide of carbon

or chloroform.* Mix the neutral or feebly acid solution in a test tube with a little of one of these fluids, sufficient to form a large drop at the bottom, then add dilute chlorine-water drop by drop, and shake the tube. With appreciable quantities of bromine, for example 1 part in 1000 parts of water, the drop at the bottom acquires a reddish-yellow tint; with very minute quantities (1 part of bromine in 30,000 parts of water), a pale yellow tint, which, however, is still distinctly discernible. A large excess of chlorine-water must be avoided, and it must always be first ascertained whether the chlorine-water mixed with a large quantity of water and some sulphide of carbon or chloroform, and shaken, will leave these reagents quite uncoloured. If not, the chlorine-water is not suited for the intended purpose. If the solution of bromine in sulphide of carbon or chloroform (ether) is mixed with a solution of potash, the mixture shaken, and heat applied, the yellow colour will disappear, bromide of potassium and bromate of potash being formed." By evaporating this solution to dryness and igniting the residue, the bromate of potash will be converted into bromide of potassium. On heating the bromide along with *peroxide of manganese* and *sulphuric acid* in a small retort, YELLOWISH-RED VAPOURS will be evolved unless the quantity be very minute. These vapours, when brought in contact with *starch paste*, will communicate to it an ORANGE-YELLOW COLOUR, which disappears on exposure to the air.†

524. Bromine in presence of iodine and chlorine may be identified by the following simple operation: mix the fluid with a few drops of dilute sulphuric acid, then with some

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* Ether was formerly employed, but it is not so well adapted as chloroform or bisulphide of carbon.

† Fresenius recommends that the fluid containing the free bromine, or the mixture of bromide, binoxide of manganese, and sulphuric acid be gently heated in a very small beaker, covered with a watch-glass with a slip of paper attached to the lower side, moistened with starch paste, and strewed over with starch powder; in the course of a short time, if bromine is present, a yellow tint will be imparted to the starch.

starch paste, and add a little red fuming nitric acid, or, better still, a solution of hyponitric acid in sulphuric acid, whereupon the iodine reaction will show itself immediately. Add now chlorine-water drop by drop until that reaction has disappeared, then add some more chlorine-water to set the bromine also free, which may then be separated and identified by means of chloroform or bisulphide of carbon, or the liberated iodine may also be taken up with chloroform or bisulphide of carbon, and chlorine-water cautiously added, when the violet-red coloration imparted by the iodine gradually fades away, and after its disappearance the brownish-yellow colour given by the bromine is distinctly visible. (*Fresenius.*)

525. Solid bromides, when distilled with BICHROMATE OF POTASH and CONCENTRATED SULPHURIC ACID, yield pure *bromine*, which becomes colourless, or nearly so, when treated with excess of ammonia; by this means it is distinguished from chlorochromic acid, which it resembles in colour.

526. If a phosphate of soda and ammonia bead, saturated with oxide of copper, is mixed with a substance containing bromine, and then ignited in the inner blowpipe flame, the flame is coloured BLUE, inclining to GREEN, more particularly at the edges. (*Berzelius.*)

HYDRIODIC ACID (HI).

527. This acid and its compounds resemble in their properties the corresponding compounds of chlorine and bromine. The pure acid is gaseous. It is extremely soluble in water, and the solution, which is colourless, resembles in properties that of hydrochloric and hydrobromic acids; but it is more easily decomposed than the two latter compounds by the substances which have an affinity for hydrogen, and also by those substances which have an affinity for the other constituent, hydrogen being set free—as mercury, for instance. The colourless solution turns speedily to a reddish-brown when in contact with the air, owing to the formation of hydriodous acid (HI_2) and water. Many of the iodides of the

heavy metals are more insoluble in water than the corresponding chlorides.

528. *Subnitrate of mercury* throws down from solutions of the iodides a yellowish-green precipitate of SUBIODIDE OF MERCURY (Hg_2I).

529. *Protochloride of mercury* throws down a red precipitate of PROTOIODIDE OF MERCURY (HgI), which is soluble in an excess of the protochloride or of iodide of potassium.

530. *Soluble salts of lead* precipitate an orange-yellow precipitate of IODIDE OF LEAD (PbI).

531. Iodine, in a free state, forms with *starch*, even in highly dilute solutions, a purple precipitate of IODIDE OF STARCH. If the iodine is in a state of combination with hydrogen or any metal, it is necessary to liberate it before applying the starch test.

532. *Chlorine gas* likewise liberates iodine from its combinations; but if added in excess, they combine together, forming a colourless compound (chloride of iodine).

533. If iodides are heated with *sulphuric acid* and *peroxide of manganese*, the iodine sublimes in the form of violet-coloured vapours, which are easily recognised.

534. Pure *nitric acid*, free from nitrous acid, decomposes hydriodic or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But *nitrous acid* and *hyponitric acid* decompose hydriodic acid and iodides with the greatest facility even in the most dilute solutions. Colourless solutions of iodides therefore acquire immediately a brownish-red colour upon the addition of some red fuming nitric acid, or of a mixture of this with concentrated sulphuric acid, or, better still, upon addition of a solution of hyponitric acid in hydrated sulphuric acid, or of nitrite of potash and some sulphuric or hydrochloric acid. From more concentrated solutions the iodine separates under these circumstances in the form of small black plates or scales, whilst nitric oxide gas and iodine vapour escape.

535. The best method of detecting iodine in a solution is

to mix with the liquid a little starch paste, and acidify it with HCl. A solution of nitr*ite* of potash* is then to be added, when, if much iodine be present, a dark blue colour will be instantly produced; if a very small quantity only—as, for instance, the two or three millionth part—then a few seconds elapse before the blue colour makes its appearance. Dr. D. Price, who invented this method states that he has, in this way, detected the $\frac{1}{4000000}$th part of iodine dissolved in water as iodide of potassium. It is, he says, much more delicate than the other tests for iodides, as well as being free from the disadvantages to which they are more or less subject. If the experiment is made in a porcelain basin, the faintest indication of colour may be observed.

536. When a solution, containing 1 part of *sulphate of copper* and $2\frac{1}{2}$ parts of *the sulphate of protoxide of iron*, is added to a neutral or slightly alkaline solution of an iodide, a white precipitate of SUBIODIDE OF COPPER (Cu_2I) is formed. The sulphate of iron is added, to convert the sulphate of copper into a subsalt. The addition of a small quantity of a solution of carbonate of soda, so as to render the solution slightly alkaline, promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent.

537. A bead of microcosmic salt, saturated with oxide of copper, if mixed with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense GREEN COLOUR to the flame.

IODIC ACID (IO_5).

538. We give as an appendix to hydriodic acid a short account of the properties of iodic acid. This acid is a white crystalline solid; it is decomposed at a moderate heat into

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* A solution of hyponitric acid in sulphuric acid may be employed in place of the nitrite of potash and hydrochloric acid. Fresenius states that a single drop on a glass rod of the hyponitric acid solution suffices to produce the reaction most distinctly.

oxygen and iodine; it is readily soluble in water. Its salts are decomposed by heat, a metallic iodide and free oxygen being formed, or into iodine, oxygen, and a metallic oxide; the alkaline iodates are the only salts of this acid which dissolve readily in water. Nitrate of silver and chloride of barium precipitate iodic acid from its solutions.

539. Sulphurous acid and hydrosulphuric acid each throw down iodine from solutions of iodic acid; if an excess of either reagent is added, the iodine becomes converted into hydriodic acid.

540. An iodate can be detected in the presence of an iodide by the simple addition of a strong acid; the hydriodic and iodic acids act upon each other in the following manner:

$$5HI+IO_5=6I+5HO.$$

NITRIC ACID (HO, NO_5).

541. The hydrate of nitric acid, when pure, is a colourless liquid, which fumes strongly in the air. It acts upon organic substances, destroying them quickly if concentrated; if they contain nitrogen, they are stained yellow by this acid. It oxidizes all the metals, with the exception of gold, platinum, and some of the rarer ones, being itself reduced to the state of nitric oxide (NO_2), which, in contact with the air, is converted into red fumes of nitrous acid (NO_4). All the oxides treated of in this work dissolve in this acid, with the exception of binoxide of tin and oxide of antimony.

542. All the neutral nitrates are soluble in water; a few basic salts are insoluble in that liquid. All the salts of this acid are decomposed by ignition, the alkaline nitrates yielding oxygen and nitrogen, and the rest oxygen and nitrous acid.

543. When nitrates are ignited in the presence of substances capable of oxidation, a portion of the oxygen passes over to them, whilst an inferior oxide of nitrogen is evolved. In some cases the combination is attended with a violent detonation; in others, vivid scintillations accompany the combustion.

544. To detect nitric acid in a solution, add to it one fourth of its volume of concentrated sulphuric acid, and *gently warm* the solution; a solution of a protosalt of iron must then be added, along with a few drops more of concentrated sulphuric acid, when the liquid will become of a deep-brown colour, attended, most likely, with an energetic disengagement of gas; the colour, in this case, will soon disappear, for a reason presently to be named, but can readily be reinstated by a fresh addition of the solution of the protosalt of iron. Or the solution of the protosalt of iron may be added first to the solution of the nitrate, and then the concentrated sulphuric acid poured in, in such a way that it forms a layer at the bottom of the test-tube; in this case the deep-brown colour will be produced at the contact-surface of the two liquids. The dark-brown colour is owing to the formation of a compound of binoxide of nitrogen (NO_2) and the protosalt of iron. This compound is destroyed by heat, with disengagement of the binoxide of nitrogen as gas—hence the fading of the colour. It may therefore be better for the young student to add the protosalt of iron when the solution of acid and nitrate is quite cold.

545. When nitrates are heated with *concentrated sulphuric acid*, in the presence of *copper turnings*, binoxide of nitrogen is evolved, which, in contact with the air, forms red fumes, owing to its conversion into nitrous acid. This experiment ought to be conducted in a narrow test-tube. The colour is best observed by looking into the test-tube lengthways.

546. If a mixture of a nitrate with cyanide of potassium in powder is heated upon platinum foil, a violent deflagration will ensue, owing to the sudden evolution of carbonic acid and nitrogen, produced by the oxidation of the cyanogen. Very minute quantities of nitrates may be detected in this way.

547. The following is an exceedingly delicate test for detecting nitric acid, it is therefore specially adapted for detecting the acid in water. Dissolve brucin in 1000 times its weight of water, pour about 15 grains of this solution into

a test-tube, then add a little of the water to be tested, and lastly some sulphuric acid; the acid is made to flow down the side of the tube so as to gather beneath the water. At the place of contact of the two liquids a rose-red zone immediately forms, if nitric acid be present in detectable quantity. The reagents must be specially purified before they can be employed. The water employed to dissolve and wash the brucin must be repeatedly rectified over potash. The brucin is washed with pure water several times to remove nitrates. The sulphuric acid is mixed with 5 per cent. of carbonate of ammonia and three fourths distilled off in a glass vessel. (*Kersten.*)

548. Dissolve 1 part of carbolic acid (phenol) in 4 parts of concentrated sulphuric acid, and dilute the solution with 2 parts of water. If the substance to be examined for nitric acid is in solution, evaporate it in a porcelain crucible or its cover, and let fall one or two drops of the phenyl-sulphuric acid solution upon the residue, at a temperature of about 212° F. By the excess of the sulphuric acid, any nitrates, if present, will be decomposed, and the nitric acid derived from them will directly form nitro-compounds with the phenol, which are indicated by the production of a reddish-brown colour. When neither organic matters, nor compounds of chlorine, iodine, and bromine, from which sulphuric acid easily separates carbon or the haloids, are present, this coloration is in itself convincing. But for fear of their presence, it is better, in all cases, to add a drop or two of strong ammonia to the coloured product, when the haloids will be dissolved in the form of colourless salts, and the carbon remain suspended in small particles, not interfering with the recognition of the characteristic yellow solution of the nitro-phenylate of ammonia. Frequently, after the addition of ammonia, there appears instead of a yellow an unstable emerald-green colour, which changes into a rose colour after the addition of an acid, and occasionally becomes greenish yellow. (*Sprengel.*)

549. When a minute quantity of *gold*-leaf is boiled in hydrochloric acid, no action is produced; but, on the addition of a little nitric acid or a nitrate, the gold quickly disappears

and may be detected in solution by the method described in par. 335.

550. When a moderately concentrated solution of potash is poured upon a mixture of zinc and iron, hydrogen is freely disengaged, even without the application of heat; if a nitrate is added to this mixture evolving the hydrogen, it is followed by an immediate development of ammonia. This reaction furnishes a good qualitative test of the presence of nitric or nitrous acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing two or three grammes of a mixture of granulated zinc and clean iron filings. A small quantity of strong potash solution is added, and the whole heated to boiling. The usual tests for ammonia may be applied at the mouth of the tube. (*Harcourt.*)

551. Very minute quantities of nitric acid may be detected also by reducing the nitric acid first to nitrous acid, which may be effected both in the moist and the dry way; in the former by treating the solution of the nitric acid or of the nitrate for some time with finely-divided zinc, best with zinc amalgam, and then filtering (*Schönbein*); in the dry way by fusing the substance under examination with carbonate of soda and carbonate of potash at a moderate heat, exhausting the mass, after cooling, with water, and filtering. Upon adding either of the filtrates to a solution of iodide of potassium mixed with starch, and dilute sulphuric acid, the fluid acquires a blue colour from iodide of starch; see pars. 534 and 535. (*Fresenius.*)

CHLORIC ACID (HO, ClO_5).

552. This acid, in its concentrated state, appears in the form of a yellow oily liquid, the odour of which resembles that of nitric acid. The dilute acid is colourless and inodorous.

553. All the chlorates are soluble in water. They are decomposed upon ignition, oxygen gas being given off and

a metallic chloride left. When heated along with organic substances, they deflagrate with far greater violence than the nitrates.

554. To detect this acid, add to a small quantity of the solid substance under examination a few drops of *concentrated sulphuric acid* in the cold. The chlorate will be decomposed, SULPHATE OF POTASH and PERCHLORATE OF POTASH (KO, ClO_7) being formed, along with a GREENISH-YELLOW COLOURED gas (chlorous acid ClO_4), which escapes. The application of heat must be avoided; and the quantities operated upon should be small, to prevent any loud and violent explosion taking place.

555. If the solution of a chlorate is coloured light blue, with some solution of indigo in sulphuric acid, a little dilute sulphuric acid added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the colour of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, and the liberated chlorine decolorizes the indigo. (*Fresenius.*)

556. Upon heating chlorates with hydrochloric acid, the constituents of the two acids decompose, forming water, chlorine, and bichlorate of chlorous acid ($ClO_3, 2ClO_5$). The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas, of a very disagreeable odour, resembling that of chlorine; the hydrochloric acid acquires a greenish-yellow colour. (*Fresenius.*)

557. If a mixture of a chlorate and cyanide of potassium is gently heated upon platinum foil, a very violent deflagration ensues, even with a minute quantity of chlorate. The experiment must only be made with very minute quantities of chlorate.

ORGANIC ACIDS.

558. Organic acids cannot be detected with the same certainty and precision as the inorganic acids. To detect with

certainty even some of those which we have given requires on the part of the analyst great skill and judgment.

559. Preliminary Examination.—A portion of the solid substance in powder must be heated nearly to boiling with concentrated sulphuric acid, except when chloric acid is present, as it would be dangerous in that case to warm the solution. We will first notice the changes produced by sulphuric acid on the inorganic acids, and then on the organic acids.

560. *Inorganic Acids.*—Carbonic acid, hydrosulphuric acid, nitric acid, hydrochloric acid, and hydrofluoric acid are evolved from the carbonates, the sulphides, the nitrates, the chlorides, and the fluorides, by concentrated sulphuric acid. The vapour of nitric acid will generally have a brown colour; the vapour of hydrofluoric acid will etch glass; and the vapour of hydrochloric acid will fume in contact with air. A greenish gas, having a smell of chlorine, will be evolved if a chlorate is present, and the solution will become yellow; vapours of bromine and iodine will be evolved if bromides and iodides are present: oxygen will be evolved if chromic acid is present, and the solution will become green; carbonic oxide will be evolved, and its presence may be proved by burning it, if cyanides or oxalates are present; it will be attended, when the latter acid is present, with carbonic acid. The other inorganic acids give off no vapours on being treated with concentrated sulphuric acid.

561. *Organic Acids.*—Tartaric, tannic, and gallic acids are immediately blackened when heated with concentrated sulphuric acid; carbonic acid is evolved at the same time from tartaric, but not from the other two. Citric and uric acids are not blackened unless boiled with the acid for some time. Benzoic, succinic, and acetic acids are not blackened by sulphuric acid under any circumstances, but they volatilize and in an unchanged state.*

562. Preparation of the Solution.—When the substance under examination is soluble in water, or if it is in solution and the fluid is water, it requires a little preparation

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* Malic acid and formic are not included in this course.

before it can be examined with advantage for the organic acids, as it conduces much to the success of the examination if no other bases but the alkalies and alkaline earths are present. In order to remove the others, the solution has sometimes to be treated with sulphuretted hydrogen and sulphide of ammonium; but *generally* it is only necessary to boil the solution with a slight excess of carbonate of soda; by this reagent all the bases but the alkalies are removed. After the solution has been boiled for some time it is filtered, and to the filtrate is added nitric acid very slightly in excess; the solution is then gently heated in order to expel the carbonic acid. After this, ammonia is added in very slight excess; and when it is required to have the solution perfectly neutral, as in testing with nitrate of silver and sesquichloride of iron, the solution, which has been rendered slightly alkaline with ammonia, is boiled in an evaporating dish until it is neutral to test-paper. When salts of ammonia are present in the substance under examination, the solution must, supposing no other bases but the alkalies are present, be boiled with carbonate of soda until all the ammonia is expelled, and the solution is then rendered neutral in the way just stated.

563. If the substance under examination is a solid and insoluble in water, but soluble in acids, it is dissolved in hydrochloric acid, if a residue remains or a solid separates from the solution it must be examined for benzoic acid according to par. 600. A saturated solution of carbonate of soda is added in excess and the mixture boiled for a few minutes, it is then filtered, and the filtrate is slightly acidified with nitric acid, and further prepared for the examination of the acids in the manner described in par. 562.

564. If the substance under examination is already in a state of solution, and the solution is acid, it must be heated with a solution of carbonate of soda, &c., in the manner described in the previous paragraph.

DETECTION OF THE ORGANIC ACIDS.

565. TARTARIC ACID.—The peculiar and highly characteristic odour which this acid evolves on ignition (575), prevents it from being overlooked if present in any quantity. But the test with acetate of potash (577) ought to be made in all cases. The solution to be examined for tartaric acid must be neutral, or if acid the free acid must only be acetic acid or tartaric acid.

566. For detecting very minute quantities of tartaric acid in large quantities of citric acid, employ also the method described in par. 589.

567. CITRIC ACID.—Before looking for this acid the presence or absence of oxalic and tartaric acid ought to have been determined; if these two last-named acids are absent, citric acid may be detected by its reaction with lime-water (588), or by its reaction with chloride of calcium in the presence of ammonia and chloride of ammonium. If tartaric acid and oxalic acid are present, they must be removed by adding chloride of calcium, ammonia, and chloride of ammonium, and time must be given for the separation of the tartrate of lime;* citric acid can then be detected by boiling the filtrate, citrate of lime precipitating.

568. BENZOIC ACID.—This acid, in the presence of succinic acid, is best detected by treating the iron precipitate of the two acids, after it has been washed, with ammonia and then filtering, and after concentrating the filtrate dividing it into two parts, mixing one part with hydrochloric acid when benzoic acid if present will be precipitated; in the other part, succinic acid is examined for by adding chloride of barium and alcohol (603).

569. SUCCINIC ACID.—This acid is best detected in the presence of benzoic acid, by the method described in the previous paragraph.

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* The separation of the tartrate of lime is promoted by agitation. The tartrate of lime is separated from the oxalate by treating the precipitate with solution of soda (579).

570. Tannic Acid.—This acid is best detected in the presence of gallic acid, by the method described at 606.

571. Gallic Acid.—This acid is best detected in the presence of tannic acid, by the method described at 611.

572. Acetic Acid.—This acid is best detected by the methods described at 616 and 620.

573. Uric Acid.—This acid is best detected by the method described at 635.

Tartaric Acid ($2HO, C_8H_4O_{10}$ or $2HO, \bar{T}$).

574. Tartaric acid occurs in the form of large colourless prisms, which are soluble in water, and have an agreeable acid taste; if the solution is kept a short time it undergoes decomposition.

575. Tartaric acid and its salts (the tartrates), when heated, char, and emit during the process a peculiar and very characteristic odour, resembling that of burnt sugar, which is best perceived when the substance is heated in a test-tube open at both ends.

576. The neutral alkaline tartrates and the tartrates of the bases of the third and fourth groups are soluble in water. The tartrates that are insoluble in water are soluble in hydrochloric or nitric acid.

577. The acid tartrate of soda is very soluble in water; but the acid tartrate of ammonia is only sparingly soluble in cold water, and the acid tartrate of potash is still more sparingly soluble in cold water, as the student will have learned in passing through the first group of bases. Tartaric acid and its acid salt he would then learn could be employed as a test for ammonia, potash and their salts; in like manner, the salts of potash, especially the acetate, can be employed as a test for tartaric acid, free and combined; for this purpose a concentrated solution of acetate of potash is added to the solution, and the mixture is then shaken very violently, as the bitartrate of potash precipitate is greatly promoted by shaking, and the

TABLE IX.

BEHAVIOUR OF THE ORGANIC ACIDS WITH THE GENERAL REAGENTS.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL AND SLIGHTLY AMMONIACAL SOLUTIONS BY CHLORIDE OF BARIUM.

Tartaric Acid, Citric Acid.

The baryta salts of these acids are soluble in dilute hydrochloric acid.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL AND SLIGHTLY AMMONIACAL SOLUTIONS *IN THE COLD* BY CHLORIDE OF CALCIUM.

Tartaric Acid.

Tartrate of lime, like borate of lime, is soluble in chloride of ammonium; it can therefore be separated from all the other inorganic acids which give precipitates with chloride of calcium, by digesting the lime precipitate in chloride of ammonium.

ACIDS WHICH ARE PRECIPITATED ON BOILING THE SOLUTION CONTAINING THE CHLORIDE OF CALCIUM.

Citric Acid.

TABLE IX.—*continued.*

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY NITRATE OF SILVER.

Tartaric Acid, Citric Acid, Benzoic Acid, Succinic Acid.

The silver salts of these acids are soluble in dilute nitric acid.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY SESQUICHLORIDE OF IRON.

Benzoic Acid, Succinic Acid, Tannic Acid, Gallic Acid.

The colour of benzoate of iron is *buff*; succinate of iron, *red brown*; tannate of iron and gallate of iron, *bluish black*.

Arsenious, arsenic, and phosphoric acids give precipitates with sesquichloride of iron, but fixed organic matter interferes with the precipitation.

ACIDS WHICH ARE NOT PRECIPITATED BY ANY REAGENT.

Acetic Acid, Uric Acid.

Acetic acid imparts to solutions of sesquichloride of iron a deep red colour.

addition of an equal volume of alcohol heightens the delicacy of the reaction.

578. *Chloride of barium* produces in solutions of the tartrates a white precipitate of TARTRATE OF BARYTA, which is soluble in solutions containing ammoniacal salts and in hydrochloric acid.

579. *Chloride of calcium* precipitates from solutions of the tartrates a white precipitate of TARTRATE OF LIME ($2CaO, \bar{T}+8$ aq.), which is soluble in acetic acid, ammoniacal salts retard the formation of the precipitate. It is distinguished from phosphate of lime, borate of lime, and oxalate of lime, by dissolving in a cold solution of caustic potash, from which solution it is precipitated on boiling, and again redissolved as the liquid cools.

580. *Lime-water* produces in solutions of the tartrates and also in solutions of the free acid, if added until the solution is alkaline, a white flocculent precipitate of tartrate of lime, which becomes crystalline after some time; this precipitate is soluble in tartaric acid and solutions of chloride of ammonium, from which solutions the tartrate of lime separates after some time in the crystalline form.

581. Acetate of lead produces in solutions of tartaric acid and the tartrates a white precipitate of tartrate of lead ($2PbO, \bar{T}$) which dissolves readily in nitric acid and in ammonia.

582. If tartaric acid (solid) or a tartrate be heated with concentrated sulphuric acid, the mixture acquires a black or a brownish-black colour, owing to the separation of carbon, which takes place simultaneously with the evolution of carbonic oxide gas.

CITRIC ACID ($3HO, C_{12}H_5O_{11}$ or $3HO, \overline{Ci}$).

583. This acid forms large transparent crystals, which are very soluble in water and have an agreeable acid taste; the solution decomposes on keeping.

584. Citric acid chars when heated; the charring is attended with an evolution of pungent fumes which cannot be mistaken for those evolved by tartaric acid.

585. Both the neutral and acid salts of the alkaline citrates are readily soluble in water; citric acid is not, therefore, precipitated from its solutions on the addition of acetate of potash. The compounds of citric acid with such of the metallic oxides as are weak bases, sesquioxide of iron for instance, are also freely soluble in water; citric acid prevents, like tartaric acid, the precipitation of alumina, sesquioxide of iron and other bases by the alkalies.

586. A solution of chloride of barium produces in solutions of the citrates a white precipitate of citrate of baryta ($3BaO, \overline{Ci}$), which is soluble in much water, in free acids, and in solutions of ammoniacal salts.

587. A solution of chloride of calcium produces in solutions of citrates, but not in citric acid, a precipitate of citrate of lime ($3CaO, \overline{Ci} + 4aq.$), which is more insoluble in hot water than cold, insoluble in potash, soluble in a cold solution of chloride of ammonium, from which it is precipitated on boiling the solution. Free citric acid must be neutralized by potash or soda before adding chloride of calcium to its solution.

588. Lime-water produces no precipitate in cold solutions of citric acid or the citrates; but on boiling the solution a precipitate is produced, which redissolves almost entirely when the liquid becomes cold.

589. If a solution of tartrate of the sesquioxide of iron is evaporated on the water-bath to a syrupy consistence, a solid basic salt is deposited, but citrate of the sesquioxide of iron under the same circumstances deposits no solid salt. Upon this difference of deportment of the iron salts of the two acids has been based a method for the detection of tartaric acid in citric acid; by this method even minute quantities of tartaric acid admit of being detected in citric acid; the following is the method:—the citric acid to be examined is dissolved in water, hydrate of sesquioxide of iron is added to the solution in excess

and the mixture is heated to about 194° F. When the acid has become saturated with oxide of iron it is filtered off from the undissolved oxide of iron. The solution is then evaporated on the water-bath to a syrupy consistence; if the citric acid contained tartaric acid, there would be formed a deposit of an insoluble basic tartrate of iron; if, on the contrary, the citric acid is pure, there is no deposit from the syrupy liquid, it remains perfectly clear.

590. A solution of acetate of lead, when added in excess, produces in solution of citric acid a white precipitate of citrate of lead ($3PbO, \overline{Ci}$) which, when washed, dissolves readily in ammonia.

591. Concentrated sulphuric acid decomposes, with evolution of carbonic oxide, citric acid, both free and combined, when in the solid state; the mixture blackens only after long boiling.

MALIC ACID ($2\,HO, C_8H_4O_8 = 2\,HO, \overline{M}$).

592. This acid crystallizes with great difficulty, and deliquesces rapidly when exposed to the air. It gradually decomposes, when exposed to a temperature of 230° F., into fumaric acid ($2HO, C_8H_2O_6$); it is decomposed, when exposed to a temperature of 392° F., into maleic acid ($2HO, C_8H_2O_6$), which sublimes, and fumaric acid, which remains behind. This experiment as a test ought to be made in a small tube, the maleic acid will first sublime and condense in the colder part of the tube, and if the temperature be raised to above 392° F., the fumaric acid will also finally volatilize and condense.

593. Malic acid forms with most bases salts soluble in water. The acid malate of potash is not very difficultly soluble in water, acetate of potash does not therefore precipitate malic acid from its solutions. Malic acid prevents, like tartaric acid, the precipitation of alumina, sesquioxide of iron and other bases by the alkalies.

594. A solution of chloride of calcium does not produce a

precipitate in solutions of the free acid or its salts until alcohol is added, when white malate of lime separates.

595. "Lime-water produces no precipitate in solutions of free malic acid, nor in solutions of malates. The fluid remains perfectly clear even upon boiling, provided the lime-water is prepared with boiling water."

596. A solution of acetate of lead throws down, from a solution of the acid or its salts, a white precipitate of malate of lead ($2\,PbO, \overline{M} + 6aq.$). If the fluid in which the precipitate is suspended is boiled, the precipitate fuses to a mass resembling resin melted under water. But this reaction is only distinctly marked when the malate of lead is tolerably pure; if mixed with other lead salts, it does not present this appearance, or at least imperfectly.

597. Concentrated sulphuric acid decomposes, with evolution of carbonic oxide, malic acid, combined as well as uncombined, when in the dry state; the mixture blackens only after long boiling.

BENZOIC ACID ($HO, C_{14}H_5O_3 = HO, \overline{Bz}$).

598. The pure acid appears under the form of white scales or needles, or simply as a crystalline powder. It is readily dissolved by alcohol and ether. It is only slightly soluble in cold water; on the addition of hydrochloric acid to an aqueous solution of any of its salts, it separates from the solution as a white crystalline powder. It volatilizes completely when heated, with partial decomposition. The fumes cause a peculiar irritating sensation, and provoke coughing. When heated in a test-tube open at both ends, a portion of the acid condenses upon the cool part of the tube.

599. Chloride of barium and chloride of calcium do not precipitate this acid under any circumstances.

600. Sesquichloride of iron produces in neutral solutions of this acid a precipitate of benzoate of sesquioxide of iron ($2Fe_2O_3, 3\overline{Bz} + 15aq.$), the colour of which is pale buff. Ammonia in excess withdraws the acid from this precipitate, hy-

drated sesquioxide of iron remaining. Benzoate of iron differs from succinate of iron in this—that it dissolves in a little hydrochloric acid, with separation of the greater portion of the benzoic acid.

601. Benzoic acid, when heated with concentrated sulphuric acid, volatilizes, but is not blackened.

SUCCINIC ACID ($2HO, C_8H_4O_6 = 2HO, \bar{S}$).

602. This acid is crystalline and volatile; it is readily soluble in water. It volatilizes without blackening when heated.

603. Chloride of barium, after the addition of ammonia and alcohol, precipitates this acid in the form of succinate of baryta ($2BaO, \bar{S}$).

604. Sesquioxide of iron, preduces, in neutral solutions of this acid, a precipitate of the succinate of the sesquioxide of iron ($Fe_2O_3, \bar{S}$), the colour of which is reddish-brown. It is decomposed in the same manner as benzoate of iron by ammonia.

605. It behaves like benzoic acid with concentrated sulphuric acid.

TANNIC ACID ($3HO, C_{18}H_5O_9 = 3HO, \bar{Q}t$).

606. This acid is a solid body, of a light straw colour, and not crystalline. It is very soluble in water; the solution absorbs oxygen from the air, which converts the acid into two others, gallic and ellagic. It is precipitated from concentrated solutions by dilute sulphuric and hydrochloric acid, in the form of a paste. It is also precipitated by dilute starch-paste, by gelatine, and albumen.

607. This acid is completely removed from its solutions by placing in the liquid a piece of animal membrane.

608. Sesquichloride of iron produces, in solutions of tannic acid or tannates, a dark blackish-blue precipitate.

609. Tartrate of antimony and potash (tartar emetic) gives in solutions of this acid a white gelatinous precipitate.

610. Concentrated sulphuric acid, treated with tannic acid or tannates in the solid state, produces a dark purplish-black liquid immediately, but does not evolve carbonic oxide.

GALLIC ACID ($2HO, C_7HO_3 = 2HO, \overline{G}$).

611. This acid crystallizes in prisms of a silky lustre, of a very pale-yellow colour. It is not very soluble in cold water, but dissolves in three parts of boiling water. Its alkaline solutions, when exposed to the air, become first yellow, then green, red, brown, and finally nearly black, which is produced by the absorption of oxygen. It is not precipitated by gelatine or animal membrane. By this behaviour it may be distinguished and separated from tannic acid.

612. Sesquichloride of iron produces, in solutions of this acid and its salts, a bluish-black precipitate. Salts of the protoxide of iron produce a black precipitate.

613. Concentrated sulphuric acid behaves with gallic acid much in the same way as with tannic acid.

ACETIC ACID ($HO, C_4H_3O_3 = HO, \overline{A}$).

614. This acid is a colourless crystalline solid below 60° F., above that temperature it is a thin colourless liquid of an exceedingly pungent and well known odour of vinegar. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. In the liquid state it has a density of 1·063, and boils at 248° F., its vapour is inflammable. On account of its solidifying below 60° F., it has received the name of *glacial acetic acid*, in contra-distinction to the mixtures of water and the acid which do not crystallize; it is to these mixtures that the name acetic acid is commonly applied.

615. All the *neutral* acetates are soluble in water; the salts of mercury and silver are the least soluble. Many of the *basic* acetates are insoluble.

616. " *If sesquichloride of iron* is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with sesquichloride of iron, the fluid acquires a deep dark-red colour, owing to the formation of ACETATE OF SESQUIOXIDE OF IRON. By boiling the fluid becomes colourless if it contains an excess of acetate, the whole of the sesquioxide of iron precipitating as a basic acetate, in the form of brown-yellow flakes. Ammonia precipitates from it the whole of the sesquioxide of iron as hydrate. By addition of hydrochloric acid a fluid which appears red from the presence of acetate of sesquichloride of iron turns yellow (difference from sulphocyanide of iron)."

617. The acetates of the alkalies and alkaline earths, when heated, yield carbonates, and, if out of contact of air, a volatile liquid of a peculiar odour, called acetone ($C_6H_6O_2$). Alkaline acetates, if mixed with an excess of alkali are decomposed into marsh gas (C_2H_4) and alkaline carbonates. Acetate of ammonia when distilled with anhydrous phosphoric acid is decomposed into water and cyanide of methyl (C_2H_3Cy).

618. Acetic acid or acetates when heated with chloride of mercury produce no precipitate of subchloride of mercury.

619. When sulphuric acid is added to acetates, the acetic acid is liberated, which is recognised by its odour of vinegar. If the acetate is distilled with the sulphuric acid, the acetic acid is obtained in the distillate.

620. When acetates are heated with about equal volumes of concentrated sulphuric acid and alcohol, acetic ether (C_4H_5O, $C_4H_3O_3$) is formed, which is readily distinguished by its characteristic odour.

621. Concentrated sulphuric acid occasions no blackening when heated with acetic acid or its salts.

622. If an excess of oxide of lead be digested in acetic acid, there is formed a soluble basic acetate of lead, which has an alkaline reaction.

FORMIC ACID ($HO, C_2HO_3 = HO, \bar{F}$).

623. This acid is a clear colourless liquid which fumes slightly in the air; it has an exceedingly penetrating odour; it boils at 209° F., and crystallizes in large brilliant plates when cooled below 32° F. Its sp. gr. is 1·235, and it mixes with water and alcohol in all proportions. When exposed to the action of heat, it volatilizes completely; the vapour is inflammable and burns with a blue flame.

624. The formiates are all soluble in water, though less so than the corresponding acetates. They are all decomposed by heat; the formiates of the fixed alkalies and alkaline earths ignited out of contact with air leave alkaline carbonates slightly blackened by charcoal, carbonic oxide and hydrogen being evolved; the formiates of other metals (copper and lead for example) when heated give off carbonic oxide, carbonic acid, and water, the metal being left in the metallic state. Formiate of ammonia when exposed to a high temperature is decomposed into hydrocyanic acid and water.

625. If sesquichloride of iron is added to a neutral formiate, the fluid acquires a blood-red colour; the liquid becomes colourless on boiling if an excess of the formiate was present, all the iron being precipitated in the form of a basic salt. The formiates, in fact, exactly resemble the acetates in their behaviour with sesquisalts of iron.

626. By the properties which this acid and its salts possess of reducing the oxides of the precious metals, it is distinguished from acetic and the other acids treated of in this work. The solution to be examined for formic acid is heated with nitrate of silver; a reduction instantly takes place, carbonic acid and water being formed.

627. If formic acid or an alkaline formiate is heated from 140° to 158° F. with protochloride of mercury, subchloride of mercury precipitates. If the mixture is heated to 212° F., metallic mercury separates along with the subchloride.

628. When dilute sulphuric acid is added to formiates, the

formic acid is liberated and is recognisable by its odour. If the formiate is distilled with the sulphuric acid, the formic acid is obtained in the distillate.

629. Upon heating a formiate with a mixture of sulphuric acid and alcohol, formic ether (C_4H_5O, C_2HO_3) is produced, which has an agreeable odour resembling peach kernels.

630. Concentrated sulphuric acid, when heated with formic acid or a formiate, decomposes the formic acid into carbonic oxide and water; there is therefore no blackening, however long the heat may be continued.

URIC ACID ($2HO, C_{10}H_2N_4O_4 = 2HO, \bar{U}$).

631. This acid occurs in delicate white needles; it is scarcely soluble at all in cold water, dilute hydrochloric or acetic acid; it is insoluble in alcohol and ether. It dissolves in concentrated sulphuric acid without apparent decomposition, and is precipitated by dilution with water. It is soluble in the alkalies and alkaline salts, from which solutions it is precipitated on the addition of acids.

632. Urates, with the exception of the POTASSIUM and SODIUM SALTS are almost all insoluble in water; the ammonium salt is extremely insoluble in water; it is however dissolved by chloride of sodium or phosphate of soda, urate of soda being formed.

633. The LIME SALT is white; the PERSALT OF IRON brown; the COPPER SALT green; the SILVER SALT white, rapidly becoming black if the liquid be heated; the MERCURY and LEAD SALTS are white.

634. Uric acid yields by destructive distillation cyanic, hydrocyanic, and carbonic acids, carbonate of ammonia, and a black coaly residue rich in nitrogen. By fusion with hydrate of potash, it furnishes carbonate and cyanate of the base, and cyanide of the alkaline metal.

635. It dissolves with the aid of heat in dilute nitric acid; the solution is attended with effervescence and evolution of red fumes, the uric acid being oxidized at the expense of the

nitric acid. If the nitric acid solution be evaporated in a porcelain dish on the water bath just to dryness, and a glass stopper moistened with strong ammonia-water be then held over the residue in the dish, a *magnificent purple colour*, owing to the formation of MUREXIDE, being produced.

636. Concentrated sulphuric acid dissolves uric acid, with the aid of heat, without change; if the heat be long continued, the liquid becomes dark.

CHAPTER V.

EXAMINATION OF LIQUIDS AND SOLIDS.

EXAMINATION OF A LIQUID.

637. The student, after he has passed through the different groups of bases and acids, in the manner previously described, commences the analysis of liquids, in which he has to look for all the different substances treated of in the work, with the exception of the organic acids.*

638. Before commencing the actual analysis, it is necessary to ascertain by preliminary experiments—1. Whether there is any solid substance in solution. 2. Whether the solution is neutral, acid, or alkaline.

639. 1st. *To ascertain whether there is any solid substance in solution.*—Evaporate, by a gentle heat, a portion of the liquid to dryness, on platinum-foil. If no residue remain, it is probably pure water, which will be further confirmed if it has no action upon test-paper. If a residue remain, which is completely volatilized when the temperature is increased, the

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* The student will find it conducive to his success in many respects, if he does not engage in the detection of organic acids until he enters upon the examination of solid substances. He will, of course, in *practice*, have always first to ascertain whether organic substances are really present or absent in a solution, before he commences the actual analysis, as the presence of fixed organic matter prevents the detection of many inorganic substances; he will likewise, in practice, have frequently to separate, by distillation, the liquid from the solid portion of a solution, in order to be perfectly certain that the fluid is *water*, and not any other liquid. This he will ascertain by examining the distilled fluid by the smell, taste, boiling point, specific gravity, &c.

only basic substances which can be present are ammonia, mercury, arsenic, and antimony. If the residue is not volatile, or at least not completely so, other substances besides these must be present. In both cases it is requisite to perform the next experiment.

640. 2nd.—The solution is examined by well-prepared test-papers, as to its neutrality, &c. Each of the three cases which may occur, and the conclusions to which they lead, are considered in pars. 641, 642, 643.

641. The solution is *neutral.* A large number of substances must therefore be absent, because the neutral salts of the greater proportion of the metals possess an acid reaction. The only salts which are neutral to test-papers are the salts of silver and manganese, and some of the salts of the alkalies and alkaline earths. The alkalies, alkaline earths, silver, and manganese are the only basic substances, therefore, which can be present; but to distinguish still further, add to a portion of the solution carbonate of soda. If no precipitate ensue, the alkaline earths and the oxides of silver and manganese must be absent; but should a precipitate be formed, all these substances may be present.

642. The solution is *acid.* The acidity may proceed from the presence of a free acid, an acid salt, or a neutral salt having an acid reaction. To ascertain to which of these causes the acidity is due, place the end of a glass rod moistened with a solution of carbonate of soda, into a portion of the fluid in a watch-glass. If the solution becomes turbid and remains so, it is due to the presence of a neutral salt; if it becomes clear again, the reaction is due either to an acid salt or a free acid. Carbonates and sulphides cannot be present in an acid solution.

643. The solution is *alkaline.* The alkalinity may proceed from an alkaline carbonate, silicate, borate, or phosphate; or it may arise from the presence of a free alkali or alkaline earth, or from the cyanogen and sulphur compounds of these metals. If the alkalinity proceeds from ammonia or its carbonate, a large number of substances (those which are in-

soluble in these reagents) must be absent. If it is due to the presence of the fixed alkalies or their carbonates, a still larger number of substances are excluded. If it is occasioned by the sulphides of the metals of the alkalies or alkaline earths, all the metals whose sulphides are insoluble in water and alkaline sulphides must be absent.

644. After the preliminary experiments have been completed, the actual analysis must be commenced, by dividing first of all the substances into groups, and these finally into individuals, as described in the former part of this work. The basic substances are first determined in analysis. When these have been discovered, correct conclusions may be drawn as to the acids which must be absent. If, for instance, baryta was found to be present in an aqueous solution, then the acids which form with it salts insoluble in water must be absent.

645. The student should never employ the whole of the solution at his disposal, but should always reserve a portion in the event of any unforeseen accident occurring, and for confirmatory experiments.

646. If the liquid under examination contains inorganic matter in suspension,* the latter, after being separated by filtration, must be brought into solution according to the methods described under the head of "Solid Substances." The solid and liquid portions ought in most cases to be examined separately.

EXAMINATION OF SOLIDS.

647. The substance is first examined as to its lustre, colour, odour, and whether it is crystalline or amorphous, since these will frequently afford a means of classifying the substance.

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* The method of preparing for analysis a solution which is thick or turbid from the presence of organic matter, is described under the head of "Solid Substances containing Organic Matter" (par. 726).

Thus, a metallic lustre will indicate probably a pure metal or an alloy. A blue colour will indicate the probable presence of some salt of copper; a crystalline structure the probable presence of a salt.

648. THE SUBSTANCE WILL EITHER BE A PURE METAL OR AN ALLOY, OR IT WILL NOT.

649. *If it is a pure metal or an alloy* treat it according to par. 729, *after* it has been examined in a glass tube closed at one end and exposed on charcoal to the reducing flame of the blowpipe.* (See pars. 652, 2nd and 4th.)

650. *If it is neither a pure metal nor an alloy, it will be free from or contain* ORGANIC MATTER which will be ascertained in making the preliminary experiment (par. 652, 2nd). *When it is destitute* of organic matter, treat it according to par. 713. *When it contains* organic matter, according to par. 726.

651. It has already been stated that the substance is submitted to different blowpipe operations before ascertaining in what liquid it will dissolve; the blowpipe operations and the order in which they are to be performed are described in the next paragraph. In these blowpipe experiments, only small quantities of the substance ought to be employed; for if too much is operated upon, uncertain results are the consequence. A particle the size of a mustard seed is sufficient, and that of the flux added about the size of a hemp seed. In reductions, a larger quantity may be employed, because, in that case, the more metal is produced, the more easily can its nature be ascertained. In all cases the substance operated upon must be reduced to the finest powder.

652. The following are the principal blowpipe operations and the order in which they are to be performed:

1st. Examine whether the substance imparts a colour to the flame, see Table page 213 and par. 656.

2nd. Examine the substance in a glass tube closed at *one* end, see Table X, and par. 666.

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* These are the only blowpipe experiments which require to be made with a pure metal or an alloy.

3rd. Examine the substance in a glass tube *open* at both ends, see par. 672.

4th. Expose the substance to the inner blowpipe flame on charcoal, see Table XI, and par. 678.

5th. Treat the substance with protonitrate of cobalt on charcoal, see Table XII, and par. 680.

6th. Examine the substance with carbonate of soda on charcoal, see Table XII, and par. 681.

7th. Fuse a portion of the substance with borax on platinum wire, see Table XII, and par. 696.

8th. Examine the substance as to its fusibility, see par. 698.

653. COLORATION OF THE FLAME.—As many substances tinge the lamp flame with various characteristic colours, the substance under examination ought to be submitted to the flame in order to ascertain the presence or absence of these substances. To obtain the colour the substance ought to be exposed to the flame on a platinum wire, and the experiment ought to be conducted in a dark room.

654. Merz, who has recently made a complete investigation of this subject, employs Bunsen's burner, and also a flame of pure hydrogen, and in addition makes use of *blue*, *violet*, *red*, and *green* glasses. The substances which he describes as giving characteristic colours to the flame of Bunsen's burner, in addition to those previously known, are nitric and chromic acids, while phosphoric and sulphuric acids give a peculiar coloration to the dark core of the flame of hydrogen.

655. The flame of Bunsen's burner gives three sorts of colour: *a*. BORDER COLOURS. These are of course peculiar only to the most volatile substances. To produce them, the loop of platinum wire is to be held outside of the flame about one or two millimetres from the lower portion of the outer limit. *b*. MANTLE COLOURS—those namely which are seen when the substance is held in the bright blue coloured mantle which forms the outer portion of the flame. *c*. FLAME COLOURS. To produce these, the loop is to be held horizontally and in the hottest part of the mantle (see par. 65). The hy-

drogen flame yields another species of colour, viz., the CORE COLOURS. These are produced only by sulphuric and phosphoric acids, which communicate respectively a blue and green tinge to the cold core of the hydrogen flame.

656. The following is a list of the substances* which colour the flame, with the colour they impart:

BLUE FLAMES.

(*Consult pars.* 657 and 658.)

Intense blue	Chloride of copper.
Pale clear blue	Lead.
Light blue	Arsenic.
Greenish blue	Antimony.
Blue mixed with green	Bromide of copper.
Blue core colour	Sulphuric acid.

GREEN FLAMES.

(*Consult pars.* 659, 660, and 661.)

Bronze-green border colour	Nitric and Nitrous acids.
„ „ „ „	Ammonia compounds.
„ „ „ „	Cyanogen „
Greenish-blue border colour	Muriatic acid.
Green mantle colour	Boracic acid.
Grey yellow-green border colour	Phosphoric acid.
Yellowish-green flame colour	Baryta.
Dark green	Iron-wire.
Full green	Copper.
Intense emerald green	Iodide of copper.
Emerald green, mixed with blue	Bromide of copper.
Pale green	Phosphoric acid.
Intense whitish green	Zinc.

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* In this list only the more commonly occurring substances are given.

RED FLAMES.

(*Consult pars.* 662, 663, and 664.)

Intense crimson	Strontia.
Reddish purple	Lime.
Violet	Potash.
Dark brownish-red border colour and a rose-red mantle colour	Chromic acid.

YELLOW FLAMES.

(*Consult par.* 665.)

Yellow	Soda.
Feeble brownish yellow	Water.

657. Blue Flames.—Copper as chloride gives an azure-blue zone, and as nitrate, a pure green flame colour. By the combined observation of both colours, copper may be distinguished from all other metals which give similar colours. The other flame colouring metals, such as arsenic, antimony, tin, lead, mercury and zinc, exhibit, especially in the form of chlorides, more or less intense bluish or greenish mantle colours, which however cannot be advantageously used as reactions for the metals themselves.

658. Sulphuric acid produces a beautiful blue core colour, being reduced to sulphurous acid. Free sulphuric acid gives the colour when the platinum loop is held in the border of the flame, but a sulphate must be held in the middle of the flame. In the latter case, it is well to dip the test into strong muriatic or fluosilicic acid.

659. Green Flames.—Nitric and nitrous acids give a bronze-green border colour, usually with an orange coloured border. The test is to be previously dried in the flame, and dipped into a solution of bisulphate of potash, or into dilute muriatic acid

according as we wish to test for nitric or nitrous acid. Compounds of ammonia and cyanogen give the same bronze-green border, but more faintly. Muriatic acid gives a very weak greenish-blue border colour, which lasts for a very short time, and therefore does not deserve attention. The acid is however decomposed into free chlorine, which may easily be recognised.

660. Boracic acid gives a beautiful green mantle colour, which is so intense that the acid may be recognised in the presence of large quantities of phosphoric acid. Borates are to be decomposed with sulphuric acid. Phosphoric acid gives a grey yellow-green border colour as well as a beautiful green core colour. The dry test is to be dipped into sulphuric acid and held in the flame in the manner already pointed out, in order to show the border colour. The green core colour is less sensitive, but indispensable in recognising phosphoric acid in the presence of large quantities of boracic acid, and is produced by alternately moistening the test with a solution of fluosilicic acid, and holding it till ignition in the hydrogen flame, until the colour distinctly appears.

661. Baryta may be recognised by the yellowish-green flame colour which appears blue green through the green glass. If the green disappears, and a red flame colour makes its appearance, the test is to be repeatedly moistened with muriatic acid, and immediately introduced while wet into the hottest part of the flame. When the blue-green colour is no longer seen, proceed to examine for lime.

662. Red Flames. Lime is present when the red flame colour, on evaporating the last portion of muriatic acid, appears siskin green through the green glass. Strontia gives in this case a weak yellow. Strontia may be recognised by the purple or rose colour which is seen through the blue glass, when the test, after moistening with muriatic acid, is evaporated to dryness in the flame.

663. Potash gives a grey-blue mantle colour, and a rose-violet flame colour. These colours appear reddish violet through the blue glass, violet through a violet glass, and blue green through a green glass. The test it to be moistened

TABLE X.

EXAMINATION OF THE SUBSTANCE IN A GLASS TUBE CLOSED AT ONE END.

(*See par.* 666.)

GASES OR FUMES ESCAPE. (*See par.* 667.)		
WATER CONDENSES ON THE SIDES OF THE TUBE		Examine whether it has an *alkaline* or *acid* reaction; if the former probably due to ammonia. (*See par.* 668.)
A sublimate is formed. (*See par.* 669.)		
Volatile Metals. (See par. 669 *a.*)	ARSENIC	The interior surface of the sublimate is crystalline. The odour of garlic is evolved.
	MERCURY	Condenses in liquid drops.
	CADMIUM	Gives a yellowish-red coating to charcoal when heated on it in the open air.
Volatile Metallic Oxides. (See par. 669 *b.*)	OXIDE OF ANTIMONY	Fuses into a yellow liquid before subliming.
	ARSENIOUS ACID	Condenses in white crystals or powder.
	ARSENIC ACID	Converted into arsenious acid and oxygen.

TABLE X—*continued.*

Volatile Salts. (See par. 669 *c.*)	AMMONIACAL SALTS	Volatilized unaltered except when the alkali is in combination with a fixed acid.
	PROTOCHLORIDE OF MERCURY	Melts before subliming.
	SUBCHLORIDE OF MERCURY	Sublimes without previous fusion.
	IODIDE OF MERCURY	Forms a yellow sublimate.
	SULPHIDE OF MERCURY	Forms a black sublimate.
	CHLORIDE OF LEAD	Fuses before it sublimes.
Non-metallic Bodies. (See par. 669 *d.*)	SULPHUR	Forms a yellow sublimate.
	OXALIC ACID	Forms a white crystalline sublimate.

The substance does not volatilize (completely).

IT LIQUEFIES. (See par. 670 *a.*)

IT BLACKENS (carbonizes). (See par. 670 *b.*)

IT CHANGES COLOUR. (See par. 670 *c.*)

with sulphuric acid, and repeatedly exposed to the flame for a short time.

664. Chromic acid gives a dark brownish-red border colour, and a rose-red mantle colour. The dry test is to be moistened with concentrated sulphuric acid, and held in the border. Oxide of chromium gives no colour, and is to be first oxidized to chromic acid by moistening with a solution of hypochlorite of soda, and drying.

665. YELLOW FLAMES.—Soda gives an orange-yellow flame colour, which in very large quantities appears blue, but in small quantities is invisible through the blue glass. Through the green glass the flame appears orange yellow, even with the smallest quantities; this glass is particularly adapted to the recognition of soda in all its compounds. The test is to be moistened with sulphuric acid, dried and held in the hottest point of the flame.*

666. EXAMINATION OF THE SUBSTANCE IN THE GLASS TUBE CLOSED AT ONE END.—The tube (see par. 81) having been thoroughly cleaned and dried, a *small portion*, in the state of powder, of the substance to be examined is introduced into it, and heated over a spirit or gas lamp, at first gently in order to ascertain whether any VOLATILE SUBSTANCES or ORGANIC MATTER form part of it; the tube is subsequently heated more strongly with the blowpipe until the glass begins to soften; for the changes consult Table X, and pars. 667 to 671.

667. GASES OR FUMES ESCAPE.—" Observe whether they have a colour, a smell, an acid or alkaline reaction, whether they are inflammable, &c.

1st. " *Oxygen.*—The disengagement of this gas indicates the presence of peroxides, chlorates, nitrates, &c. A glimmering slip of wood is relighted in the gaseous current.

2nd. " *Sulphurous acid.*—This is often produced by the decomposition of sulphates, it may be known by its peculiar odour and by its acid reaction.

3rd. " *Hyponitric acid*, resulting from the decomposition of nitrates, especially with oxides of the heavy metals; it may be known by the brownish-red colour of the fumes.

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* For this description of flame coloration I am indebted to Merz's paper on the subject.—R. G.

4th. "*Carbonic acid.*—The evolution of carbonic acid indicates the presence of carbonates decomposable by heat. The gas evolved is colourless and tasteless, non-inflammable; a drop of lime-water on a watch-glass becomes turbid on exposure to the gaseous current.

5th. "*Carbonic oxide gas.*—The escape of this gas indicates the presence of oxalates and also of formates. The gas burns with a blue flame. In the case of oxalates the carbonic oxide evolved is generally mixed with carbonic acid, and is therefore more difficult to kindle; in the case of formates the evolution of the gas is attended with marked carbonization. Oxalates evolve carbonic acid when brought into contact with binoxide of manganese, a little water, and some concentrated sulphuric acid, on a watch-glass; formates evolve no carbonic acid under similar circumstances.

6th. "*Cyanogen.*—The evolution of cyanogen gas denotes the presence of cyanides decomposable by heat. The gas may be known by its odour, and by the crimson flame with which it burns.

7th. "*Hydrosulphuric acid gas.*—The escape of hydrosulphuric acid gas indicates the presence of sulphides containing water; the gas may be readily known by its odour.

8th. "*Ammonia* resulting from the decomposition of ammoniacal salts, or also of cyanides or nitrogenous organic matters, in which latter case browning or carbonization of the substance takes place, and either cyanogen or offensive empyreumatic oils escape with the ammonia."—Fresenius's 'Chemical Analysis.'

9th. *Nitric acid, fluorine, chlorine, bromine and iodine.*—The detection of these in the preliminary examination is best effected by mixing the substance under examination with rather more than its own weight of *fused bisulphate of potash,* and then heating the mixture in a glass tube closed at one end, before making the examination the student ought to consult pars. *a*, *b*, *c*.

a. Nitric acid.—If a nitrate is present, nitrous fumes are disengaged, the colour of which may be best perceived by looking directly down the neck of the tube, inasmuch as a thicker stratum of the gas is in this way seen.

b. Fluorine.—According to Berzelius the substance ought, for the examination of fluorine, to be mixed with four times its weight of fused bisulphate of potash, and the tube, after the introduction of the mixture, strongly heated with the blowpipe flame until sulphuric acid begins to be evolved, and in order to avoid too great frothing up, the mass should be heated from the top downwards. If fluorine is present, the tube will be encrusted more or less with silica deposited from the fluosilicic acid gas which passes off. The lower extremity of the tube containing the fused mass is then cut off, and the upper part rinsed out with water and dried with blotting-paper. If much fluorine is present in the substance operated upon, the glass tube will be dull all over its inner surface, but if a small quantity only is present, the corrosion will be only partial.

c. Iodine, bromine and chlorine.—Violet fumes of iodine are evolved, along with sulphurous acid, on heating a substance containing a compound of iodine with bisulphate of potash in the tube; some of the iodine is generally deposited as a black sublimate on the upper part of the tube. Bromine and chlorine are in like manner evolved from their compounds.

668. AQUEOUS VAPOURS ARE GIVEN OFF.—The water may have existed either mechanically, or as water of crystallization, or as constitutional water. If the body decrepitates on ignition, the decrepitation is due probably to the presence of an anhydrous salt which contains water mechanically between its crystalline plates and the expulsion of which gives rise to the decrepitation. If the water is present as water of crystallization, the crystalline body will generally fuse during the expulsion, and resolidify after it; some substances swell considerably during the expulsion—borax and alum for example. If the water comes from some decomposable hydrate, the substance will not fuse during its expulsion.

669. A SUBLIMATE IS FORMED.—The sublimate may be due

to some volatile metal, metallic oxide, volatile salt or non-metallic body:

a. The volatile metals are principally arsenic, mercury, and cadmium, these metals form a black or grey sublimate having more or less of a metallic lustre. *Arsenic* is sublimed not only when it exists in its free state, but also from some metallic arsenides, which are decomposed by heat into arsenic and an arsenide containing a less quantity of arsenic; a few arsenites also yield metallic arsenic when heated out of contact with the air. *Mercury* may be sublimed from most of its compounds; if the quantity is inconsiderable, it may only yield a gray sublimate; the globules can sometimes be rendered apparent by touching the sublimate with a glass-rod, or on examining the sublimate with a lens. *Cadmium* may be sublimed from some of its alloys; it may be recognised by heating it in contact with the air when it becomes converted into the brownish-yellow oxide.

b. VOLATILE METALLIC OXIDES.—Oxide of antimony first fuses into a yellow liquid, and then sublimes under the form of shining crystalline needles. The sublimate of arsenious acid may either be in the form of shining crystals or in the form of a white powder which the magnifying glass reveals however to be crystalline.

c. VOLATILE SALTS.—*Ammoniacal salts* form white sublimates; heated with soda and a drop of water on platinum foil, they evolve ammonia. *Protochloride of mercury* begins to melt at a very gentle heat and then sublimes; *subchloride of mercury* sublimes without previous fusion; the sublimate has a yellowish tinge whilst hot, but is perfectly white when cold. *Iodide of mercury*, which is red, yields a yellow sublimate which becomes red by trituration. *Sulphide of mercury* gives a black sublimate which acquires a red tint when rubbed. When compounds of mercury are mixed with soda, and then heated in the tube a sublimate of mercurial globules will be obtained. *Chloride of lead* first fuses and then sublimes. The sublimate of sulphide of arsenic may be easily mistaken for pure sulphur.

d. NON-METALLIC BODIES.—*Sulphur* sublimes in reddish-brown drops, which solidify on cooling, and turn yellow or yellowish brown. The sulphur may be present merely in the state of mixture, or it may be combined with some metal which abandons a portion of it when heated out of contact of the air. *Oxalic acid* yields a white crystalline sublimate attended with thick fumes; the sublimate when heated on platinum foil with a drop of concentrated sulphuric acid gives rise to a copious evolution of gas.

670. THE NON-VOLATILE MATTER. The non-volatile portion of the substance may liquefy, carbonize, or merely change colour:—

a. If it liquefies without expulsion of aqueous vapour and resolidifies when the heat is removed, the liquefaction may be due to various substances, as chloride of silver, the alkaline nitrates and chlorates, &c. If by intense heat, oxygen is evolved, and if a small piece of charcoal on being thrown into the fused mass is readily consumed, *nitrates* and *chlorates* are indicated.

b. If it carbonizes organic matter is present. "Carbonization is always attended with evolution of gases (acetates evolve acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with the alkalies or alkaline earths."

c. It changes colour. "From white to yellow, turning white again on cooling, indicates *oxide of zinc;* from white to yellowish brown, turning to a dirty light yellow on cooling indicates *binoxide of tin;* if the colour changes from white to brownish red, turning to yellow on cooling, and the body is fusible at a red heat, this indicates the presence of *oxide of lead;* if the colour changes from white, or pale yellow, to orange yellow, or to a deeper and more reddish tint up to reddish brown, becoming pale yellow on cooling, and the body fuses at an intense heat, this indicates the presence of *teroxide of bismuth;* if the colour changes from red to black, turning reddish brown again on cooling, this indicates the presence of *sesquioxide of iron;* if the colour changes from yellow to dark orange, and the body fuses at an intense heat, this indicates *neutral chromate of potash*, &c."

671. In case of the non-appearance of any of these reactions it must not be always concluded that the above-mentioned bodies are entirely absent; for sulphur and arsenic may be present in such forms that the simple application of heat will either not sublime them or will expel them in combinations which afford none of the distinctive characters of the simple bodies; moreover, two or more of these may be present together in a substance, and afford sublimates having mixed characters, so that the individual elements are difficult to distinguish. Such is frequently the case with arsenic and sulphur, which together, form a coating on the tube having a metallic lustre at its lower extremity, and passing upwards successively into black, brown, red, and finally yellow—these colours being due to combinations of sulphur and arsenic, which are more volatile than metallic arsenic; therefore, the examination of a substance in the glass tube affords frequently no positive indication of the presence of a body, but merely intimates its probable existence, to establish which further investigations are necessary. Such intimations are, however, of importance, as they serve as guides in after-processes.

672. EXAMINATION IN THE OPEN TUBE.—A small particle of the substance, in powder, is introduced into the tube (see par. 80) at about half an inch from its extremity, and gradually heated, the tube being held in a slightly inclined position, so that a current of air may pass fully through it. By this means the substance is roasted, or oxidized, and various matters contained in it are volatilized and pass off up the tube.

673. The roasting must be performed slowly, with a gradually increasing temperature, and with a good current of air* passing through the tube, otherwise unoxidized matter may be

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* By inclining the tube more or less, we have the means of regulating the current of air; very little passes through the tube when it is held in a horizontal position, but it becomes more and more active as the tube is held more and more vertically.

volatilized and the mineral substance clotted and fused together. If a perfect roasting be required, the substance, after being heated for some minutes in the tube, is shaken out into an agate mortar, remixed and roasted, and this process is repeated until fumes are no longer evolved. (Consult pars. 674 to 677.)

674. Almost all *metallic sulphides* disengage on roasting sulphurous acid; some sulphides yield besides a sublimate of sulphur. Sulphurous acid may be recognised by its odour or by its decolorizing moistened brazil-wood paper,* a strip of which ought to be introduced in the interior of the raised end of the tube.

675. Fluorine.—Very minute quantities of fluorine can be detected by the following method:—"Microcosmic salt, which has been previously fused upon charcoal or platinum, is finely powdered and mixed with some of the substance to be examined also finely pulverized. A portion of the mixture is introduced into an open glass tube, and the blowpipe flame so directed upon it, that a part of the flame passes up the tube. By this means, hydrated hydrofluoric acid is formed (if the substance be free from silica), which passes up the tube and may be recognised both by its peculiar pungent smell and by the mode in which it corrodes the sides of the glass tube, rendering them dull and opaque wherever any moisture condenses. If Brazil-wood paper moistened be exposed to the action of the gases passing up the tube, it will be coloured yellow, affording another indication of the presence of fluorine. If the substance also contains silica, fluoride of silicon will be formed, which also colours yellow moist Brazil-wood paper, and is decomposed by water,† silica being formed, which, as the water evaporates, is deposited on the sides of the tube, and is clearly perceptible either with or without the aid of a lens. If now the tube be washed out with water and dried, it will be generally found

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* Prepared by moistening slips of fine printing-paper with decoction of Brazil wood.

† Water will be present owing to the products of the combustion of the lamp passing up the tube.

corroded by the fluorine, which leaves a dull spot wherever it attacks the glass. As this experiment requires the application of a strong heat, so that the glass tube is frequently softened and bent, thus interfering materially with the success of the experiment, *Smithson* has recommended a piece of platinum foil to be bent into the form of a gutter and inserted to about half its length into the glass tube; the mixture of the fused microcosmic salt and the substance under examination is laid upon the projecting part of the platinum, and the flame so directed upon it that the products of combustion pass up the tube. This arrangement has the advantage that the fused substance does not come in contact with the glass tube, and the inconveniences attending the fusing and softening of the glass are altogether avoided.

676. A sublimate may be formed in the second operation when none has been formed in the first, as oxide of bismuth will be formed when the sulphide or an alloy of bismuth (scarcely any sublimate is produced on roasting bismuth itself) is present in the substance under examination, and sulphate of lead will be formed if the sulphide of that metal is present; in like manner, arsenious acid and oxide of antimony will be formed if an arsenide or an antimonide is present. If the fumes formed have an odour of garlic it shows the presence of arsenic.

677. All the sublimates which are formed by oxidizing substances in the open tube are white, but the coloured substances which are volatilized in the closed tube are still more easily volatilized in the open tube; for it need scarcely be observed that most of the reactions produced in the closed tube are also produced in the open one.

678. EXAMINATION ON CHARCOAL.*—Most of the reactions described in pars. 667 to 675 are also produced on the charcoal; but only those reactions which are special to this operation are noticed in Table XI and text.

679. In addition to the points which require to be attended to, as pointed out in the table, it should be particularly noticed

* Consult pars. 73, 74, 75, and 76, before commencing the operation.

whether the substance disengages a peculiar odour, as arsenic and sulphur might be detected by the odours they produce;* and it should also be noticed whether the substance fuses; the oxides and acids which fuse are the oxides of antimony, bismuth, lead, and oxide of copper. "Most metallic sulphurets fuse when heated before the blowpipe upon charcoal, and this effect often takes place with sulphurets of metals, the oxides of which are infusible; but many of these sulphurets become rapidly oxidized during the operation, and exhale an odour of sulphurous acid in the same way as when heated in the open tube, and are thus converted into metallic oxides. Most metals fuse before the flame of the blowpipe; and all of them, except those called noble, are subsequently oxidized by the exterior flame."

After this examination is complete, the substance must still be retained on the charcoal for the examination with protonitrate of cobalt.

680. TREATMENT WITH PROTONITRATE OF COBALT.—No explanation beyond that given in Table XII is required.

681. EXAMINATION WITH CARBONATE OF SODA ON CHARCOAL.—The substance (in powder) under examination is mixed with an equal quantity of carbonate of soda, and the mixture is made into a paste with a drop of water. After it has been dried at a moderate heat, it is exposed on the charcoal to the reducing flame of the blowpipe, the oxidizing flame spreading over the charcoal. (See Table XII, and pars. 682 to 695.) Should no reduced metal make its appearance, after exposure for two or three minutes to the flame, a little cyanide of potassium may be added, and the experiment continued for two or three minutes longer. Many of the metallic arsenides and sulphides require to be carefully roasted, and thus deprived of their arsenic and sulphur, and the metals themselves oxidized, before they can be reduced by carbonate of soda; in this case, the residue which remains from the open-tube experiment can be employed. It must be remembered, how-

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* It must be remembered that charcoal becomes, on exposure to the blowpipe flame, covered with a *bluish-white ash.*

TABLE XI.

EXAMINATION ON CHARCOAL. (See par. 678.)

If deflagration ensue, the presence of a *chlorate* or *nitrate* is indicated.

Substances which volatilize or pass off in vapour.	*Substances which are not volatilized.*		
Mercury, Arsenic, Cadmium, Antimony, Zinc, Ammonia, Sulphur, and Lead partly.	Silver, Copper, Bismuth, Lead, Tin, Gold, Platinum, Cobalt, Nickel, Manganese, Iron, Aluminum, Chromium, Barium, Strontium, Calcium, Magnesium, Sodium, Potassium, Silica, &c.		
Colour of the different Sublimates.	Substances which yield *coloured incrustations.*	Substances which are *infusible, but become luminous.*	Substances which *fuse, or run into the charcoal.*
Mercury, Zinc, Ammonia . White. Antimony, white, imparting a greenish-blue colour to the flame. Cadmium . . . . Red brown.	Lead, Bismuth, } Yellow.	Alumina, Baryta, Strontia, Lime, and Magnesia *and their salts.*	Salts of the fixed Alkalies.

TABLE XII.

BLOWPIPE OPERATIONS.

Heat the substance on CHARCOAL, with the blowpipe flame; then moisten it with a solution of PROTONITRATE OF COBALT: again strongly heat it in the *outer flame.* (See par. 680.)	
Substances which yield *coloured masses* when thus treated.	
OXIDE OF ZINC	Green.
ALUMINA, SILICIC ACID, PHOSPHATES,	Blue.
MAGNESIA	Pink.
BINOXIDE OF TIN	A bluish-green colour.

Mix the substance with *Carbonate of Soda,* and expose the mixed mass to the inner blowpipe flame, on CHARCOAL. (See pars. 681 to 695.)	
Oxides and Combinations of Oxides which can be reduced to the *metallic state.*	
Oxide of	*Character of the Metal.*
BISMUTH	Brittle.
ANTIMONY	Brittle; volatilizes in white fumes, yielding an incrustation.
SILVER	Malleable; very white.
TIN	Malleable.
LEAD	Malleable, very.
COPPER, GOLD,	Well known colours of the metals.
NICKEL, COBALT, IRON,	These three are reduced, but yield no metallic beads; they are rendered magnetic, and can therefore be at once distinguished from the rest.

Heat the substance before the blowpipe on PLATINUM WIRE, with a bead of BORAX. (See pars. 696 and 697.)	
Substances which give *coloured beads.*	
In the outer flame.	
COPPER, COBALT,	Blue.
NICKEL	Reddish.
IRON	Yellow.
MANGANESE	Amethyst.
CHROMIUM	Green.
In the inner flame.	
COPPER	Red.
COBALT	Blue.
NICKEL	Gray.
IRON	Green.
MANGANESE	Colourless.
CHROMIUM	Green.

To discover the reduced metal, remove the fused mass from the charcoal, and grind it up in a small mortar with water; allow it to stand a minute, and then pour off the water and the suspended matter in it, and continue to repeat the process until the metal remains at the bottom of the mortar, perfectly free from charcoal, &c. If it is brittle, it will be in the state of very small spangles; if malleable, it will have adhered to the mortar or pestle, or a portion of it, whilst the rest may be in large spangles.

ever, that cadmium as well as sulphur and arsenic may have been expelled by the roasting.

682. The metals which can be reduced by this means, besides gold, platinum, and silver, are lead, antimony, tin, copper, zinc, bismuth, nickel, cobalt, iron, cadmium, arsenic, and mercury. "Gold, silver, copper, and tin compounds, yield metallic beads, but no incrustations; iron, nickel, cobalt, and platinum compounds give neither beads nor incrustations; bismuth, lead, and cadmium compounds produce a yellow or brown deposit on the charcoal; antimony and zinc give a white incrustation;* arsenic may easily be recognised by its odour."

683. If a globule has been obtained, it is necessary to ascertain whether it is malleable or brittle: "for this purpose, it is allowed to cool perfectly, and carefully removed with a pair of tweezers. Having been placed upon a little anvil,† and struck with a small hammer—or, if these two blowpipe instruments are not at hand, upon the bottom of a strong mortar—and struck sharply with the pestle, when, if brittle, it of course falls to powder (as in the case of antimony); if semi-malleable, it flattens out, at the same time breaking into several pieces (as with bismuth); and if fully malleable, flattens out without breaking (like lead).‡

684. "*The globule obtained is malleable.*—Lead (makes a black streak upon paper); a yellow incrustation is formed upon the charcoal. Tin; a slight white incrustation. Copper (known by its colour). Silver.

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* The ash of the charcoal may sometimes be mistaken by beginners for a sublimate, but it may be distinguished from such by remaining unaltered before the inner flame.

† The anvil is a small block of hardened steel about two inches square and three quarters of an inch thick, polished upon one or more of its faces. The hammer is made of hardened steel, one face must be square with sharp edges, for trying the malleability of substances, and the opposite end should be bevelled off like a chisel to detach small fragments of minerals, &c.

‡ To prevent the fragments from dispersing from the striking they may be folded in a piece of thin paper, the corner of which may be held during the operation.

685. "*The globule is semi-malleable.*—Bismuth; a yellow incrustation.

686. "*The globule is brittle.*—Antimony; abundant white incrustation.

687. "*If no metallic globule* is obtained, but shining *metallic spangles* are observed after levigation; probably tin, antimony, or copper."

688. Magnetism. — To ascertain whether the reduced metal is magnetic, an ordinary steel magnet must be presented to it; if any of the metallic particles are magnetic they will adhere to it. The trial may be made with far more delicacy by bringing the metallic particles near a magnetic needle which is supported on a centre, which it turns on.

689. Only one mineral, magnetic oxide of iron, possesses magnetic *polarity* and *attraction*, all other minerals which are attracted by the magnet, possess attraction only. The magnetic character serves to distinguish a few of the mineral species, which otherwise have very close resemblances; especially, magnetic iron ore from specular iron, and magnetic pyrites from common pyrites.

690. Many minerals become attractable by the magnet, only after undergoing the high heat of the blowpipe; this is the result of a partial decomposition.

691. Cupellation.—This is the process of separating gold and silver from other substances by heat, and obtaining them in a state of purity. The following is Berzelius' method:

692. "A small quantity of bone-ashes (in powder) is to be taken on the point of a knife, moistened with the tongue, and kneaded in the palm of the left hand, with a very little soda, into a thick paste. A hole is then made in a piece of charcoal, and filled with the paste, and its surface smoothed by pressure with the agate pestle. It is then to be gently heated by the blowpipe till perfectly dry (the soda only assists the cohesion, and may be omitted). The assay,* previously fused with *pure* lead, is placed in the

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* It would be better to roast the substance under examination with carbonate of soda on charcoal before assaying it with the pure lead.

middle of this little cupel, and the whole heated by the exterior flame. When the operation is finished, the precious metals are left on the surface of the cupel. This experiment is so delicate that grains of silver, visible to the naked eye, and, indeed, such as may be collected by the forceps and extended under the hammer, may in this way be extracted from the lead met with in commerce.

693. "If the button obtained by cupellation does not possess the colour of gold, but appears white, the quantity of gold is less than that of silver, in which case, the button should be placed in a porcelain capsule, a few drops of nitric acid poured on it, and the capsule heated over the lamp.

694. "If the button does not contain more than a fourth part of its weight in gold, it becomes completely black, and then decomposes, the silver being dissolved, while the gold remains in black flakes. When the silver button contains more than a fourth of its weight of gold, it is blackened, but the silver is not dissolved. It is neither blackened nor dissolved, if the proportion of gold to silver is nearly equal; in this case the button must be melted with twice its bulk of pure silver, on charcoal, and again heated with nitric acid, by which the mass becomes black, and dissolves; the pure gold being left behind."

695. If the substance fuses into a transparent glass with the carbonate of soda, it shows the presence of silicic acid, par. 508.

696. TREATMENT WITH BORAX.—To obtain a bead of borax, one end of the platinum wire is bent into a small hook. This is heated in the blowpipe flame, and then dipped into the borax; a small portion of the borax will adhere to it; and this being fused in the flame, and, while hot, dipped again into the powdered borax, a fresh quantity will adhere, which is fused as before; and this continued until a bead of the requisite size is obtained. A great many metallic oxides dissolve in borax, forming coloured glasses. If any metallic arsenides or sulphides are present, it is necessary to roast the substance in the way previously described (672) before making the examination with borax; and it is frequently advantageous, before roasting the

powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

697. While the bead of borax is still hot, it is touched with a small quantity of the powder of the substance under examination, and that which adheres is fused into it. The operator must then observe—1st, whether the substance is soluble or insoluble in borax; and 2nd, the colour of the borax bead in (1) the oxidizing flame, and (2) in the reducing flame, both in the hot and in the cold state. In performing this experiment, care must be taken not to dissolve up, in the first instance, too large an amount of the oxide or other substance under examination. If a small quantity afford no distinct reaction, more may be easily added. If, however, the colour of the bead is too intense to be clearly distinguished, the bead may be jerked off the wire, and that which still adheres fused up with a fresh quantity of borax, by which a paler and more transparent glass will be obtained.

698. Examination in the Platinum Forceps.—"If the operator has convinced himself by a preliminary experiment that the substance under examination does not, when heated, attack platinum,* a small splinter of it is to be taken between the platinum forceps, and subjected to the oxidizing flame; but if the substance is very fusible, a piece of platinum wire, hooked at one end, may be used instead of the forceps. If, however, the substance be one which exerts a chemical action on platinum, and would therefore injure the forceps or wire, charcoal must be employed as the support.

699. "In order to test the fusibility of a mineral, a small splinter, having a sharp edge or point, should be broken off and held in the forceps at a short distance beyond the point of the inner blue flame, so that the sharp edge is strongly heated. If a gas flame be employed, the mineral must be held somewhat further from the point of the blue flame than is necessary in the case of an oil-lamp, in order to prevent any reduction taking place, which would materially interfere

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* Platinum cannot be employed when compounds of the easily reducible metals, as silver, and lead, are present.

with the results. If a powdered substance is to be tested, or one which decrepitates when heated, and which must therefore be previously pulverized, the following process may be resorted to:—A small quantity of the powder is made into a paste with water, and spread upon a piece of charcoal; it is then dried, and strongly heated with an oxidizing flame, it will then (generally) cohere sufficiently to allow of its being taken up between the forceps and tested in the usual manner. Care must be taken that the substance, if a fusible one, and one which acts upon platinum, does not fuse upon the platinum points of the forceps.

700. "Of the metallic oxides, the following only are fusible in the oxidizing flame, viz., the oxides of copper, lead, antimony, and bismuth. Metallic sulphides are, with few exceptions, readily fusible under the blowpipe flame; these exceptions are sulphide of zinc and sulphide of manganese."

701. "Of the simple silicates, *i. e.* silicates with a single base, those of the alkalies are most fusible. The silicates of lime and those of magnesia are with a few exceptions practically infusible, the most fusible being, according to *Berthier*, those in which, as in Wollastonite, the oxygen of the acid is double that of the base. Silicates of alumina are infusible.

702. "Of the silicates of iron those of the protoxide and magnetic oxide are very fusible, but those of the peroxide are practically infusible. Consequently, under the blowpipe flame, the fusibility of a silicate of iron much depends upon whether it be submitted to the oxidizing or the reducing flame; for the silicates of the peroxide infusible in the former become fusible and magnetic in the latter. If, therefore, a substance be infusible, or only very slightly fusible in the oxidizing flame, it may afterwards be submitted to the extremity of the reducing flame, since many substances infusible in the former become fusible on undergoing a partial reduction.

703. "The fusibility of a compound silicate, *i. e.* a silicate containing two or more bases depends upon that of the simple silicates of which it is composed, but is generally greater than the mean of these latter. Thus many silicates of lime and

magnesia, and of lime and alumina are more fusible than any of the simple silicates which enter into their composition.

704. "According to their relative fusibility, minerals may be classified as follows:

I. Readily fusible to a bead.
II. With difficulty fusible to a bead.
III. Readily fusible on the edges.
IV. With difficulty fusible on the edges.
V. Infusible.

705. "In testing the fusibility of a mineral substance, it should be noticed whether, if fusible, a clear or opaque bead is obtained; also, whether the substance changes colour, becomes magnetic, or exhibits any phenomena of intumescence, ebullition, &c., all of which are useful characters in indicating the nature of the mineral."

706. "The degree of fusibility is a very important point to ascertain, when the examination in question refers to the native *combinations of silica* and certain other *minerals*, for this characteristic feature displayed by the blowpipe is often the only one by which we may distinguish those which consist of earths, and which contain no notable quantities of metallic oxides, properly so called. Amongst the minerals most frequently met with, the following are infusible:

Quartz,
Corundum,
Tourmaline (both that which contains alumina and even that which contains soda),
Zircon,
Cyanite,
Phenakite,
Leucite,
Talc,
Pyrophyllite,
Apatite,
Gehlenite,
Apophyllite,
Staurotide,
Refractory clays,
Hydrate of alumina,
Hydrate of magnesia,
Sulphate of alumina,
Carbonate of lime,
Carbonate of magnesia,
Carbonate of zinc,
Allophane,
Spinel,

Pleonaste,
Gahnite,
Olivine,
Cerite,
Cymophane,
Gadolinite (which, being heated, becomes suddenly luminous, as if it caught fire),
Vitreous tin,
Rutile,
Titanic iron,
Tantalite,
Turquoise,
Titaniferous oxide of iron,
Chrome iron,
Native oxides of iron,
Yttrotantalite,
Dioptase,
Chondrodite,
Topaz.

707. "Amongst those which are almost infusible and only become rounded at the edges, the following may be named:

Felspar,
Albite,
Petalite,
Labradorite,
Anorthite,
Nepheline,
Tubular spar,
Pyroxène (which contains much magnesia),
Epidote (which intumesces by the first impression of the heat),
Euclase (which intumesces by the first impression of the heat),
Emerald,
Titanite,
Sodalite,
Calcareous Scheelin,
Meerschaum,
Soapstone,
Serpentine,
Mica (some species, especially those found in granite),
Dichroite,
Heavy spar,
Celestine,
Gypsum,
Apatite,
Fluor spar.

708. "The following are fusible:

Zeolites (most of them intumesce),
Spodumene (which intumesces),
Mejonite (which froths up before fusing),
Elæolite,
Amphibole (most of which boil up whilst in fusion),
Pyroxène (those which contain no excess of magnesia),

Idocrase (intumesces in fusing),
Garnet,
Cerine,
Orthite (boils in fusing),
Ferruginous Scheelin,
Boracite,
Hydroboracite,
Datholite,
Botryolite,
Cryolite,
Mica (several species, especially those which contain lithia),
Tourmaline (those which contain potash),
Axinite (intumesces whilst fusing),
Amblygonite,
Lazulite,
Haüyne,
Nosin,
Eudialyte,
Pyrosmalite."—*Rose's Manual of Analysis.*

709. *When the student has completed the preceding preliminary experiments, he will be able to arrange the substance under examination* UNDER ONE OF THE THREE FOLLOWING DIVISIONS:

710. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER. See par. 713.

711. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER. See par. 726.

712. THE SOLID IS EITHER A PURE METAL OR AN ALLOY. See par. 729.

713. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER.

714. Before a solid can be acted upon by reagents, it must be brought into a state of solution. For this purpose it is submitted to the action of different fluids, and the one in which it dissolves is termed its solvent. The solvents employed in qualitative analysis are water, hydrochloric, nitric

and nitro-hydrochloric acids. Water, when it can be employed, is always to be preferred.

715. The student must particularly guard against adding too much of the solvent, especially if it be an acid. To avoid this, he must add it in small quantities at a time, and apply heat after each addition. The substance should, before being submitted to the action of solvents, be reduced to the state of a very fine powder, and fifteen or twenty grains employed for the analysis. The whole of the substance must, however, never be employed, but always a portion kept in case of any unforeseen accident, or for confirmatory experiments.

716. The powdered substance is boiled in ten times its amount of water. *It all dissolves.*—Make the preliminary experiments described under the head of Liquids, and then proceed with the actual analysis. *A portion remains undissolved.*—Filter a few drops of the liquid, and evaporate them to dryness on platinum foil. If a large residue remains on evaporation, the whole of the solution must be filtered, and submitted to analysis. The insoluble residue, after being well washed with boiling water, must be examined according to 717. If no residue remains on evaporating the aqueous solution, or at all events a very slight one, pour the remainder of the water off, and treat the insoluble substance according to 717.

717. The substance which was partly or entirely insoluble in water, is boiled in concentrated hydrochloric acid.* *It all dissolves.*—Add to the solution the water which was poured off, and then proceed with the analysis. *A portion remains undissolved.*—Ascertain if anything has dissolved, by evaporating a portion of the fluid to dryness on platinum foil. Should this be the case, place the tube, with its contents, on one side, and proceed with the next experiment.

718. A fresh portion of the original substance is boiled in

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* If hydrochloric acid causes any effervescence, the evolved gas must be examined for carbonic, hydrosulphuric, and hydrocyanic acids, as directed under the "General Properties of the Acids."

concentrated nitric acid. *The substance dissolves.*[*]—Remove as much of the free acid as possible by evaporation; dilute the concentrated solution with water, and then proceed with the analysis. *It does not dissolve.*—Allow it to settle; pour off one half the acid, add a like quantity of concentrated hydrochloric acid, and again boil. If a portion still remains undissolved, return to the strong hydrochloric acid mixture (717); filter, and analyse the filtrate in the usual way. The residue insoluble in acids, after being well washed, must be treated according to 719.

719. The usually occurring substances, which are insoluble in water and acids, are the sulphates of baryta, strontia, lime and lead, alumina, peroxide of iron and their phosphates, the chlorides of silver and lead, fluoride of calcium, silicates, silica, and sulphur.

720. A small portion of the residue, insoluble in water and acids, is heated on a slip of platinum foil. If sulphurous acid is evolved along with the volatilization of the whole of the substance, sulphur only can be present. When other substances are present, add to another small portion a drop of sulphide of ammonium. If the colour remains white, silver, lead, and probably iron, are absent.

721. A small quantity of the dry residue, in the state of a very fine powder, is mixed with four times its weight of carbonate of soda and potash. The mixed mass is placed in a platinum crucible,[†] and heated over a Berzelius spirit lamp for about half an hour; or, what is still better, the platinum vessel is placed within a Hessian crucible containing a little

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[*] If the substance dissolves with the separation of a light-yellow coloured mass of sulphur, it points out the presence of a sulphide. When nitric acid is employed as the solvent, as much of the free acid as possible ought to be removed by evaporation, before passing hydrosulphuric acid gas through the solution, as they decompose each other, the decomposition being attended with the separation of a large amount of sulphur.

[†] The compounds of the easily reduced metals, such as silver, lead, &c., must not be fused in platinum vessels, as they form alloys with that metal, which greatly injures or altogether destroys the platinum vessel: porcelain crucibles must therefore be employed in such cases.

carbonate of magnesia, and exposed to a full red heat, for the same length of time, in a furnace. The magnesia is employed to prevent the platinum from coming in contact with the Hessian crucible.

722. On cooling, the fused mass is boiled with water, and filtered. The filtrate is to be examined for the *acids* and *alumina*, the residue for the *bases*.

723. *Examination of the filtrate.*—To one portion of the filtrate add hydrochloric acid until the solution is distinctly acid; evaporate to dryness, and ignite until acid fumes are no longer evolved. To the dried mass add dilute hydrochloric acid, and boil; if a residue remains, silicic acid is present. To the filtrate from the silica add ammonia in excess, and then warm the solution; if a precipitate is formed, it must be due either to alumina or its phosphate. After having filtered and washed the precipitate, examine it for alumina and phosphate of alumina, according to Table V. In the filtrate from the alumina precipitate, or in the solution which has failed to give a precipitate, test for phosphoric acid by adding chloride of ammonium, and then sulphate of magnesia. Acidulate another portion of the original filtrate with hydrochloric acid, and examine for sulphuric acid by adding chloride of barium. Another portion must be acidulated with nitric acid, and tested for chlorine by nitrate of silver. To detect fluorine, an examination must be made according to 500 or 501.

724. *Examination of the residue.*—After having removed all the substances soluble in water, by repeated washings, dissolve the residue, if lead and silver are absent, in hydrochloric acid, and proceed with the analysis in the usual way. If the residue does not completely dissolve in the acid, and the two metals just named are absent, it shows that a portion of the substance has not been decomposed. When this is the case, filter off, and examine the filtrate.

725. When the fixed alkalies are to be looked for in the insoluble residue, another portion, in fine powder, must be mixed with about four times its weight of carbonate of baryta, and fused in a platinum crucible, in the manner already de-

scribed. On cooling, the fused mass is digested with dilute hydrochloric acid, and filtered. The filtrate is evaporated to dryness, and ignited; the dry residue must be treated with water, and again filtered. The filtrate, after being freed from iron, alumina, baryta, lime, and magnesia, must be evaporated to dryness, to expel the ammoniacal salts which have been employed in their precipitation; if a residue remains, it must be examined for potash and soda.

726. THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER.

727. The presence of fixed organic matter* interferes with the detection of many substances. Thus, in the presence of tartaric acid, which is a fixed organic acid, the oxides of aluminum, chromium, and iron, and many other metallic oxides, are not precipitated by the alkalies; alkaline citrates prevent the precipitation of acids, by bases, with which the acids form insoluble salts under ordinary circumstances; a soluble salt of baryta will not produce a precipitate, even in a solution of a sulphate, if an alkaline citrate be present, unless the sulphate is present in the proportion of three or more equivalents for every one of the citrate. It is therefore necessary, after precipitating the fifth and sixth groups by hydrochloric acid and sulphuretted hydrogen, to destroy the fixed organic matter, when it is present, which will have been ascertained in the preliminary examination. For this purpose, the filtrate from the sulphuretted hydrogen precipitate, or the solution which has failed to give a precipitate with this reagent, is evaporated to dryness and ignited† until all the organic matter has been

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* Organic substances are termed *fixed* when they cannot be distilled or volatilized without decomposition. The organic matter ought to be tested for nitrogen; for this purpose it is mixed with caustic in powder or with soda-lime, and the mixture heated in a test-tube, when, if it contains nitrogen, ammonia will be evolved.

† Many substances, especially alumina and oxide of iron, after ignition dissolve with very great difficulty even in the concentrated mineral acids.

destroyed, the residue must then be dissolved in water and acids, and examined in the regular way.

728. Sometimes we are obliged to have recourse to the following method for destroying the organic matter, especially in the case of solutions which have to be examined for *poisons*:—The solid substance or solution is boiled with concentrated hydrochloric acid, to which chlorate of potash, in powder, is added gradually until the mixture becomes perfectly fluid; the solution is then heated until all free chlorine is evolved, after which it is diluted with water and filtered. The filtrate must be examined in the regular way. The residue must be examined for chloride of silver.

729. THE SUBSTANCE UNDER EXAMINATION IS A PURE METAL OR AN ALLOY.

730. Nitric acid behaves with metals in the following manner:—Gold and platinum are neither dissolved nor altered in the least degree by it. Tin and antimony are converted by nitric acid into oxides, which do not dissolve in or combine with an excess of the acid. The other metals are oxidized and converted by it into soluble nitrates. On account of the different behaviour, therefore, which nitric acid exhibits with the metals, it is usual to employ it as the solvent of alloys, &c.

731. To the metal or alloy under examination, which is placed in a small flask, is added concentrated nitric acid, and heat applied. One of the three following cases will then occur:—1. Complete solution takes place. 2. A white insoluble substance separates. 3. A metallic residue remains. Each of the three cases are considered separately in detail.

732. 1. *If complete solution ensues,* GOLD, PLATINUM,* TIN, and ANTIMONY† must be absent. After removing the

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The residue may therefore require protracted boiling in acids, although the original substance dissolved in water or dilute acid very readily.

* Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

† Very minute traces of antimony are often completely dissolved by nitric acid.

greater part of the free acid by evaporation, dilute the solution with water,* and proceed with the analysis in the regular way. Mercury, if present, will be found in the state of protoxide.

733. 2. *If a white insoluble substance separates*, TIN or ANTIMONY is indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and proceed with the filtrate in the ordinary way. The precipitate, after being well washed with water, is treated with a hot concentrated solution of tartaric acid. If it all dissolves, TIN is absent. The presence of ANTIMONY is confirmed by hydrosulphuric acid producing in the tartaric acid solution, to which hydrochloric acid has been added, an orange-red precipitate. If the whole of the *insoluble substance* does not dissolve in tartaric acid, the solution is filtered. The filtrate is examined for antimony by the method just stated. The residue, after being well washed, is mixed with carbonate of soda and cyanide of potassium, and exposed on a charcoal support to the inner blowpipe flame. If tin is present, ductile metallic grains will be obtained.

734. 3. *If a metallic residue remains*, GOLD or PLATINUM is indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and examine the filtrate in the usual way. The metallic residue is dissolved in aqua regia. One portion of the solution is tested for GOLD by means of protosulphate of iron (335). The other portion is tested for PLATINUM by means of chloride of potassium (338).

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* If the solution becomes turbid on the addition of water, it indicates the presence of bismuth.

APPENDIX TO PART I.

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735. **Bunsen's blowpipe experiments.**—The relative quantity of potash, soda, and lithia can be approximatively determined in the various alkaline silicates as well as the recognition of the silicates, if the reaction of the specimen, both before and after the addition of *gypsum* (see par. 145), be compared with a standard series of silicates the proportion of alkali in which is known.

736. The process adopted in these cases will be most readily understood by an example. Bunsen selects the discrimination of the following minerals:—Orthoclase and its varieties, Sunadin and Adularia; Leucite, Labradorite; Albite and Oligoclase, Anorthite, Nepheline, Hauyne, and Lasurstein; Petalite, Lepidolite, and Triphane. These are divided into two groups—those containing *litha*, and those which do not contain that alkali. It is first ascertained to which of the two groups the sample belongs, by exposing it with gypsum in the melting-space side by side with a specimen of pure potash, and viewing the two flames through the indigo prism. If the sample contains lithia, its flame at that part of the prism at which the soda colour vanishes appears red against the cornflower-blue of the potash. With thicker layers of indigo, the red of the litha gradually lessens in intensity, while the cornflower-blue of the potash passes through violet into red, which, with a certain thickness of the indigo layers, is quite like the colour of the litha. If no litha is found, the sample belongs to the first group; in the other case, to the second.

737. The individual minerals of the first group are recog-

nised by comparing them with each other according to their relative proportions of potash and soda. A standard series of felspathic minerals is selected, and arranged according to the soda they contain. Bunsen uses the following series, and distinguishes them by the numbers placed over the analyses:

	1 Lasurstein.	2 Nepheline.	3 Albite	4 Orthoclase.	5 Sunadin.	6 Labradorite.	7 Anorthite.	8 Leucite.
NaO	9·09	15·44	10·06	7·08	4·0	2·55	1·13	
KO	—	4·94	—	7·03	8·0	1·06	0·62	22
MgO	—	—	0·34	—	—	0·33	0·97	
CaO	3·53	1·77	—	0·48	1·0	12·02	17·22	
MnO	—	MnO, Fe_2O_3 0·65	0·25					
Fe_2O_3	FeO, 0·86	—	0·95	0·63	0·6	FeO, 0·66	1·50	
Al_2O_3	31·76	33·28	18·65	19·99	18·5	34·66	30·50	23
SO_3	45·58	44·03	67·75	65·19	66·6	48·62	48·75	54
SO_3	5·89							
Cl	0·42							
S	0·95							
HO	0·12	0·21	—	0·38	—	0·49		

738. These silicates are heated, powdered, and arranged according to their numbers, in small bottles. If one of these standard silicates, and the sample to be tested, either with or without gypsum, be simultaneously placed side by side in the melting-space, so that, besides the tests themselves, small but equal lengths of the platinum wire are ignited, the iodide of mercury paper before the flame appears more or less bleached. If the sample be now removed from the flame, and the paper exhibits a distinct passage to red, the sample contains more soda than the standard silicate; if the paper is white, the reverse is the case. By ascertaining in this manner between what two of the silicates the reaction falls, the proportion of soda in the silicate under examination can be approximatively determined to a few per cents.

739. Although these quantitative estimations of soda can be made quickly and without difficulty, yet there are a few precautions which must not be neglected, to prevent mistakes arising. The specimens to be compared (the test specimen and the standard silicate) must be as nearly equal as possible, as regards quantity, which is measured by the eye; and then

care must be taken that the lengths of the platinum wire in the flame are also equal; but, above all, the eye must be accustomed to distinguish the different brightnesses of the same tint from the changes in colour, which are very different. Inasmuch as the eye is not susceptible enough for the more intense bleaching of the iodide of mercury, in cases when the bleaching is intense the paper must be illuminated so strongly by the flame of an ordinary candle, that a colour nearer to the red, but at the same time white, is produced.

740. There is no *quantitative* blowpipe test for potash so accurate as that for soda. It suffices for all purposes to distinguish, according to the duration and intensity of the potash colouring a *slight*, a *strong*, and a *very strong* potash reaction. The flames produced by oligoclase, orthoclase and leucite, are used as the deciding points of comparison. The silicate to be tested for potash is mixed with gypsum, and one of the standard potash silicates is also mixed with gypsum in the same way as in testing for soda. The substance under examination, and the standard silicate after gypsum has been added, are placed in the melting-space of the flame, and in such a manner that the coloured flames arising from them appear to the naked eye of the same size and appearance. The flames are then viewed through the indigo prism. The sample containing more potash is distinguished by greater dimensions, more intense colour, and longer duration of the red flame, as well as by the occurrence of the blue and violet colour in thinner layers of the solution. The following is a scheme of the behaviour of the above-mentioned standard silicates—

		Without Gypsum.	With Gypsum.
Lasurstein Nepheline	1 2	NaO: 1 more than 2. KO: not to be detected. 1 and 2 fusible.	NaO: 2 more than 1. KO: both very feeble and equal.
Nepheline Albite	2 3	NaO: 2 more than 3. KO: not to be detected. 2 and 3 fusible.	NaO: 2 more than 3. KO: 2 more than 3.
Albite Orthoclase	3 4	NaO: 3 more than 4. KO: not to be detected. 3 and 4 fusible.	NaO: 3 more than 4. KO: 4 stronger than 3.
Orthoclase Sunadin	4 5	NaO: 4 more than 5. KO: not to be detected. 4 and 5 fusible.	NaO: 4 more than 5. KO: 5 scarcely more perceptible than 3.
Sunadin Labradorite	5 6	NaO: 5 more than 6. KO: not to be detected. 5 fusible in a bead. 6 fusible on the edges.	NaO: 5 more than 6. KO: 5 more than 6.
Labradorite Anorthite	6 7	NaO: 6 more than 7. KO: not to be detected. 6 fusible at the edges. 7 fusible to a globule.	NaO: 6 more than 7. KO: scarcely to be detected. 6 more than 7.
Anorthite Leucite	7 8	NaO: 7 about equal to 8. KO: not to be detected. 7 fusible to a globule. 8 infusible.	NaO: 7 more than 8. KO: 7 scarcely to be detected. 8 very strong.

741. The reason that lasurstein, which only contains 9 per cent. of soda, gives a stronger soda reaction than nepheline, which contains 15 per cent., is that it already contains sulphuric acid, and can therefore only be compared with silicates containing no sulphuric acid when these are fused with gypsum, when, as is seen from the table, the anomaly disappears. One must be certain that the substance under examination contains no sulphuric acid, chlorine, and fluorine, as these substances, by giving rise to the formation of volatile soda compounds, render the reaction more delicate. Those silicates containing sulphuric acid are placed in a group by themselves, and compared in a similar way to the felspars, by the assistance of a special reagent scheme. The detection of sulphuric acid in the silicates is effected by fusing a sample of the silicate with soda in the reducing flame, letting it cool in the dark part of the flame, and then testing it on polished silver. Chlorine and fluorine are tested for in a similar manner.

742. In testing a sample, a splinter is brought into the flame, and by the intensity of the bleaching of the iodide-paper the place is approximatively determined. To come nearer to the number, a lighted candle is approached to the iodide-paper, and the distance observed at which the bleaching passes into red. The nearer the candle can be placed, the lower in the series is the silicate. With lasurstein, the candle can be brought within two or three inches without producing red. After this preliminary test, two, or at most three, comparative observations will show the place of the silicate.

743. Lithia silicates must be tested for separately. The above soda scale cannot be used, as the lithia flame gives rays which redden the iodide-paper; this is not the case with potash. Lithia silicates can only be compared amongst themselves; and lepidolite, petalite, and triphane are best used as reagents. Their deportment is as follows:

1 *a Lepidolite.*—Easily fusible. In the oxidizing flame, yellowish red to the naked eye; in the reducing flame yellow; with the indigo prism a strong, and with gypsum a still stronger, lithia reaction; tolerably strong potash reaction, still stronger with gypsum and the prism. Feebler soda reaction than 2 *a* and 3 *a*. The varieties richer in fluorine often give a stronger soda reaction than 2 *a* and 3 *a* especially with gypsum.

2 *a Petalite.*—Pretty readily fusible, with intumescence; no potash reaction; feeble soda reaction; with gypsum, stronger than 3 *a*, and feebler than 1 *a*. Otherwise like lepidolite.

3 *a Triphane.*—Fuses without intumescense. Only with gypsum a feeble soda reaction, which is feebler than 2 *a*. On the other hand, a stronger lithia reaction than 2 *a*. Otherwise like petalite.

744. The following is the composition of the minerals used in these reactions—

	1 *a.* Lepidolite.	2 *a.* Petalite.	3 *a.* Triphane.
LiO	2·41	3·30	5·47
NaO	0·71	1·19	0·46
KO	8·60	——	0·14
MgO	0·53	——	0·15
CaO	——	——	0·50
MnO	1·24	——	——
FeO	14·57	——	trace
Al_2O_3	17·62	18·58	29·14
SiO_3	48·65	77·79	65·02
F	6·16	——	——

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745. METHOD FOR THE DETECTION OF VERY MINUTE QUANTITIES OF BISMUTH, ARSENIC, AND ANTIMONY IN METALLIC COPPER. About 200 grains of the metal are dissolved in nitric acid, a small quantity of a solution of nitrate of lead is added, equal to about ten grains of the salt, and subsequently an excess of ammonia and carbonate of ammonia. A precipitate is formed, which may consist of oxide and carbonate of lead, arseniate and antimoniate of lead, and oxide of bismuth, the whole of the copper remaining in solution. The precipitate is separated by filtration, thoroughly washed, and digested in a strong solution of oxalic acid, whereby the antimony and arsenic are dissolved, whilst oxalate of bismuth and oxalate of lead remains undissolved; examine the dissolved portion according to *a* and the undissolved portion according to *b*.

a. To the filtered liquid, sulphide of ammonium is added, or, what is preferable, it is rendered alkaline by ammonia, and hydrosulphuric acid is passed through to saturation. Traces of sulphide of copper generally impart a brownish tinge to the liquid, and are deposited after some time, as it is nearly impossible to wash away the last traces of that metal from the nitrate of lead precipitate. This sulphide is filtered off, and a slight excess of hydrochloric acid is then added to the filtrate, which is diluted to about eight ounces. If any large amount of either antimony or arsenic be present, there will be an immediate precipitate. If smaller quantities exist (one- or two-hundredths of a grain) the flask should be placed on the sand-bath for a few hours, and the temperature maintained at from 140° to 200° F., when the metals, if present, will make their appearance as sulphides. If the precipitate be orange or orange-red, the presence of antimony is certain, but if of a pure canary-yellow, its absence may be presumed.

The precipitated sulphides are oxidized by means of concentrated nitro-hydrochloric acid, the clear solution is mixed with chloride of ammonium, excess of ammonia and sulphate of magnesia, when the arsenic is precipitated as arseniate of magnesia and ammonia. The filtrate from this precipitate is slightly acidified with dilute hydrochloric acid, and the antimony is precipitated by hydrosulphuric acid.

b. The undissolved portion is dissolved in as small a quantity as possible of dilute hydrochloric acid; considerable excess of iodide of potassium is introduced into the hydrochloric acid solution, and the liquid is warmed until the precipitate disappears. On cooling, the crystalline scales will show by their colour, the presence or absence of bismuth (355). (*Abel and Field.*)

PART II.

CHAPTER VI.

ANALYSIS OF ORGANIC SUBSTANCES.

746. All organic substances contain CARBON; a large number are composed of CARBON and HYDROGEN only; a still larger number contain OXYGEN in addition to the two last-named elements; and a large number are composed of CARBON, HYDROGEN, OXYGEN and NITROGEN. A smaller number contain SULPHUR in addition to these four elements, and a still smaller number contain PHOSPHORUS.* Organic substances, therefore, unlike inorganic ones, are all composed of some two, three, four, or five elements, and these elements are the same for all the different organic bodies. But although the formation of organic substances is restricted to some three, four, or five of the elementary bodies, their atomic constitution is far more complex than that of mineral substances, and this is one of the most marked distinctions between organic and inorganic bodies. For example, "a particle of common salt, or of cinnabar presents a group of not more than two atoms, whilst an atom of sugar contains thirty-six elementary atoms, and the smallest particle of olive oil consists of several hundred simple atoms.

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* It is still doubtful whether phosphorus exists in any natural anim or vegetable substances in an unoxidized state.

747. "It is upon the greater complexity of composition of organic bodies, together with the lesser force with which, consequently, their constituent atoms attract each other, that their easier decomposability depends: heat, for example, disturbs their composition with much greater facility than it does that of inorganic bodies. The atoms of the former, once put in motion, or by the action of heat being separated to a greater distance from each other, arrange themselves into less complex atoms, in which the force of attraction acts in fewer directions and in which it is consequently able to oppose a proportionably stronger resistance to the further action of causes of disturbance,—decomposition."—*Liebig.*

748. Organic compounds may be analysed either with a view simply to resolve them into their *proximate constituents*, as, for instance, resolving wheat flour into its proximate constituents, starch, sugar, gluten, ligneous fibre, and oily matter; this kind of analysis is called the *proximate analysis* of organic substances; or the analysis may have for its object the mere testing the organic compound for some one or two elements, as nitrogen and sulphur; this is called *elementary or ultimate analysis.**

749. We will first describe the method of testing organic substances for nitrogen, sulphur, phosphorus, and inorganic substances,† and afterwards describe the proximate analysis of organic substances.

ELEMENTARY ANALYSIS.

750. *Test for an organic compound.*—As all organic substances contain carbon, and as they do not contain oxygen in

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* By means of quantitative ultimate analysis we determine the *relative proportions* of the constituent elementary atoms and also their *absolute quantity*, that is, we determine the exact number of equivalents of carbon, hydrogen, oxygen, &c., which constitute the equivalent of the analysed compounds.

† Animal and vegetable substances are frequently composed of inorganic as well as organic compounds, and it is as necessary to determine the nature of the inorganic as of the organic matter.

sufficient quantity to combine with the whole of their carbon and hydrogen, it follows that if they are heated in a closed vessel, as a small glass tube, so as to exclude the air, a black or carbonized residue will remain.* No inorganic compound leaves a residue of carbon when heated under similar circumstances.

751. *Tests for Nitrogen.*—Substances containing a tolerably large quantity of nitrogen, emit in burning the familiar smell of singed hair or feathers; if this smell is distinctly perceptible, no further test is required to confirm the presence of this element. When there is no distinct smell of burnt feathers, one of the two following tests may be employed:

1st. The substance to be examined, which must be in the solid state, is mixed with solid *hydrate of potash* or with *soda-lime*,† the mixture is introduced into a dry test-tube, and then ignited; if the substance contains nitrogen, ammonia will be evolved on ignition, and may be detected in the usual way (Table 1, A 2, page 55). This method of examining organic compounds for nitrogen is based upon the circumstance that, when organic substances containing nitrogen in an *unoxidized state*, are ignited with hydrate of potash or soda, the water of hydration is decomposed, the oxygen uniting with the carbon of the organic body, and forming with it carbonic acid, whilst the hydrogen at the moment of its liberation enters into union with the nitrogen of the substance, and forms with it ammonia; the following changes, for instance, would take place in igniting cyanogen with an alkaline hydrate or soda-lime—

$$C_2N + 4HO = 2CO_2 + NH_3 + H$$

2nd. "Lassaigne has recently proposed another method which is based upon the property of potassium to form cyanide of potassium when ignited with a nitrogenous organic substance. The following is the best method of performing the experiment:

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* Volatile bodies require a different method of treatment for detecting their carbon, but as these do not come within the scope of this work we shall not enter upon the method for detecting carbon in such substances.

† Soda-lime is a mixture of caustic-lime with hydrate of soda, it is the water in combination with the soda which is the acting agent; the lime is simply employed to prevent the soda from fusing.

"Heat the substance under examination, in a test-tube, with a small lump of potassium, and after the complete combustion of the whole of the potassium, treat the residue with a little water (cautiously); filter the solution, add two drops of solution of sulphate of protoxide of iron containing some sesquioxide, digest the mixture a short time, and add hydrochloric acid in excess. The formation of a blue or bluish-green precipitate or coloration proves the presence of nitrogen (516).

"Both methods, 1st and 2nd, are delicate; the 1st is the one most generally employed; it fully answers the purpose in nearly all cases.

3rd. "If, however, the nitrogen exists in the organic compound in an oxidized state, it cannot be detected by either of the methods just given, but it may readily be detected by heating the substance in a tube, when the evolution of red acid fumes, imparting a blue tint to iodide of starch paper, will incontestably prove it."

752. *Tests for sulphur.*—If the substance is in the solid state, it may be mixed with about twelve times its weight of pure solid hydrate of potash, and about six times its weight of pure nitrate of potash; or it may be intimately mixed with some pure nitrate of potash and carbonate of soda; the mixture is then heated to fusion in a crucible. The fused mass is allowed to cool, then dissolved in water, the solution acidified with hydrochloric acid and tested subsequently for sulphuric acid with chloride of barium.

753. Fluids are treated with fuming nitric acid, or with a mixture of nitric acid and chlorate of potash, at first in the cold, finally with heat; the solution is then tested for sulphuric acid with chloride of barium or nitrate of baryta.

754. As the two methods just described serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that element may be present, we give another method (755),

which serves to detect only the sulphur in the non-oxidized state in organic compounds.

755. Boil the substance with a strong solution of potash, and evaporate nearly to dryness. Dissolve the residue in a little water, pour the solution into a flask,* and slowly add dilute sulphuric acid through the funnel-tube, if sulphur is present the *lead test-paper* will turn brown.

756. *Tests for phosphorus.*—The methods described in pars. 752 and 753, will likewise serve for phosphorus. The solutions obtained are tested for phosphoric acid either according to par. 484, 487, or 488. If the method described in par. 753 has been employed the greater part of the nitric acid must be removed before the test for phosphoric acid is employed.

757. *Test for inorganic substances.*—"A portion of the substance under examination is heated on platinum foil, to see whether or not a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance under examination occupies on the platinum foil, to the most intense redness, directing the flame of the blowpipe upon the corresponding point of the lower surface of the foil." The methods for examining the residue are described in pars. 762 to 773.

PROXIMATE ANALYSIS OF ORGANIC SUBSTANCES.

758. Organic substances, like inorganic ones, are either acids, bases, salts, or indifferent bodies; and the resolution of organic compounds into their proximate constituents, is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavours to separate (by solvents, application of heat, &c., &c.), the indi-

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* The flask must be provided with a funnel-tube which is fitted into a cork, on the under surface of the cork is attached a slip of paper which has been thoroughly moistened with a solution of acetate of lead, and then touched with a few drops of a solution of carbonate of ammonia.

vidual constituents from one another, either in the *direct* way, or after having previously converted them into appropriate forms.

759. Of the solvents employed in organic analysis ether is particularly valuable as a solvent for fatty substances, and for caoutchouc and camphor; alcohol, for the solution of many crystallizable organic principles, such as the vegetable alkalies; whilst water dissolves sugar, gum, starch, and other bodies, which are nearly insoluble in alcohol and ether. In some cases benzole, in others chloroform, is a valuable solvent, and may be substituted for ether, which they most resemble in their solvent action. In particular cases dilute acids, and in others dilute alkalies may be employed, but they must be used with caution, as they are liable to act not merely as solvents, but also to produce important chemical changes upon the compounds submitted to them. No general rule can be laid down for the extraction of the different proximate principles, each class of substances requiring special modifications, which experience alone can indicate.

760. In all cases of proximate analysis, the employment of the microscope will be found invaluable as a means of watching the progress of the separation of the various principles, and of ascertaining whether the substances which the chemist has isolated are mixed with other bodies which may resemble them in chemical habitudes. When a substance or deposit assumes the crystalline state, such an examination, by revealing the similarity or difference in form of its component particles, is often more valuable for ascertaining the purity of a substance than ordinary chemical reagents.—*Miller.*

761. We shall now give the method for the examination of the ash, whether derived from animal or vegetable substances, and we shall then give under Animal and Vegetable Chemistry, the properties and reactions of the chief organic compounds of animal and vegetable origin, and along with this the proximate analysis of mixed animal substances and the analysis of urine.

EXAMINATION OF THE INORGANIC CONSTITUENTS OF ANIMAL AND VEGETABLE SUBSTANCES.

762. *Preparation of the ash.*—The incineration of the substance* is best effected by placing it in a platinum dish, or other shallow vessel, and introducing the vessel into a muffle, which should then be gradually heated; but not carried beyond a very faint redness.† For merely qualitative analysis it will generally be found sufficient to char the substance in a porcelain or platinum dish, with the aid of a wide glass tube or lamp-glass to increase the draught. "The heat must always be moderate to guard against the volatilization of certain constituents, more especially of metallic chlorides. It is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as *e. g.* the ash of beetroot molasses, it is even advisable at first, simply to char the mass in a crucible at the lowest possible temperature, then to treat with water until the principal portion of the soluble salts is extracted, afterwards dry the residue, and finally, incinerate it in the muffle" (*Fresenius*). Alkaline sulphates are frequently converted by the reducing action of carbon, into sulphides and hyposulphites. The ashes of animal substances often contain cyanates, which are best destroyed by moistening the ashes with water, and then gradually heating to redness; one moistening is usually sufficient to convert them completely into carbonates.

763. *Analysis of the ash.*—In the qualitative examination it is usual to examine the aqueous solution, the hydrochloric acid solution, and the portion insoluble in acids separately—supposing the ash is not entirely soluble in water—as we thereby obtain a better acquaintance with its general character, and

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* Before incinerating the substance care must be taken to free it from all adhering impurities as these are frequently attached to plants.

† Substances to which this mode of incineration is unsuited, are charred first at a gentle red heat in a large covered platinum or Hessian crucible, and the charred mass is subsequently incinerated in the muffle.

the state or condition in which the constituents are present. In this examination we shall confine ourselves to the natural constituents of the ashes of plants and animals; if accidental constituents require to be sought for, a complete qualitative inorganic analysis, according to the methods given in Part I of this work, must be undertaken.

764. The following are the natural constituents:

Bases.	*Acids.*
Oxide of iron.	Silica.
Oxide of manganese.	Phosphoric acid.
Lime.	Sulphuric acid.
Magnesia.	Carbonic acid.
Soda.	Chlorine.
Potash.	Fluorine.
Lithia.*	Iodine.†

765. Boil the ash with water, filter, and examine the filtrate according to next par., and the portion insoluble in water after it has been well washed according to par. 769.

766. *Examination of the aqueous solution.*—Add to about one-half the aqueous solution hydrochloric acid, if effervescence ensues, it may be due to carbonic acid, sulphuretted hydrogen or hyposulphurous acid; examine the evolved gas for carbonic acid according to par. 436; the other two gaseous acids need not be attended to, as they, if present, are only due to the reduction of the alkaline sulphates (475).

767. Evaporate the solution, which has been acidulated with hydrochloric acid, to dryness, treat the residue with hydrochloric acid and water; if a portion remains undissolved it is due to silicic acid, in this case filter and add to the filtrate, or to the solution if there is no silicic acid, ammonia slightly in excess, and then acetic acid in excess, and then a drop of sesquichloride of iron (487) if a precipitate is produced, phos-

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* Lithia has lately been found in the ash of many plants; Rubidium has also been found, but this can only be discovered by spectrum analysis.

† Iodine and bromine need only be looked for in marine plants.

phoric acid is present, in that case add more sesquichloride of iron until the solution is of a slightly reddish colour. Boil the solution whether phosphoric acid is present or not, in order to get rid of the iron which has been added; when all the iron has been precipitated, which is known by the complete decoloration of the liquid, filter, and to the filtrate add ammonia and oxalate of ammonia, if, after allowing the liquid to stand for some three or four hours a precipitate is formed, lime is present;* filter and divide the filtrate into two parts, to one part add ammonia and phosphate of soda, if a precipitate is formed after some time, magnesia is present. Evaporate the other portion of the filtrate to dryness, and ignite to get rid of and burn off all carbonaceous matter, examine the residue for soda (147), for potash (142), and for lithia (157).

768. Add to a portion of the aqueous solution, which has not been acidified, nitrate of silver as long as a precipitate continues to form; warm gently, and then cautiously add ammonia; if a black residue is left, this consists of sulphide of silver, proceeding from a sulphide or a hyposulphite. Mix the ammoniacal solution now—after previous filtration if necessary—cautiously with *pure* nitric acid in slight excess, to effect the solution of the precipitate of phosphate of silver formed, thus leaving only chloride (iodide, bromide) of silver undissolved. Filter, and examine the precipitate as directed (428), if it is likely iodine or bromine, or both, can be present, but if it is certain from the nature of the substance that these elements must be absent, the precipitate need not be examined further, as it can only be due to chloride of silver. Neutralize the filtrate exactly with ammonia; if on the neutralization, a *bright yellow* precipitate is produced, the phosphoric acid

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* If carbonic acid is found to be present, lime and magnesia must of course be absent, when this is the case, divide the filtrate from the silicic acid precipitate into two portions, test one for phosphoric acid by adding chloride of ammonium, ammonia and sulphate of magnesia (484), and test in the other portion for soda, potash, and lithia, in the manner directed in pars. (142, 147 and 157).

present is the tribasic acid, but if the precipitate is *white*, the phosphoric acid is either bibasic or monobasic acid. (See par. 486.)*

769. Warm then the portion of the ash insoluble in water, with hydrochloric acid, if effervescence ensues it indicates carbonic acid combined with lime or magnesia; if chlorine is evolved it denotes the oxides of manganese.

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* At par. 486 we have noticed that if a phosphate contains three atoms of fixed base, the fluid, after the complete precipitation of the phosphoric acid by means of nitrate of silver, will be neutral, but if it contained only two atoms or one atom of fixed base, the fluid after the precipitation of the acid with the silver salt, will be acid. Further, tribasic phosphate of silver ($3AgO, PO_5$) is yellow, whilst bibasic ($2AgO, PO_5$) and monobasic (AgO, PO_5) phosphate of silver are white. Again, a tribasic phosphate containing two atoms of fixed basic is converted by ignition into a bibasic phosphate; and a tribasic phosphate containing one atom of fixed base is converted by ignition into a monobasic. We will now see how Liebig employed these facts in his investigation into the constitution of the ash of the juice of the flesh from different animals:

Liebig found that the ash of the juice of the flesh in the case of the ox, horse, fox, and roe-deer, gave with water a strongly alkaline solution, and that it was precipitated, first white, then yellow, by neutral nitrate of silver; and the mixture, after complete precipitation, was perfectly neutral. This proves that the ash contains a *bibasic* alkaline phosphate and a *tribasic* alkaline phosphate. When this ash was mixed with nitric acid, dried up, and again ignited (by which means the chlorine of the alkaline chlorides was expelled), and the metals added to the phosphates in the form of oxides, the proportion between the *white* and the *yellow* precipitate with nitrate of silver was altered, the quantity of the yellow precipitate being increased; but the two colours of the precipitate were constantly observed.

The ash of the juice of the flesh of fowl, Liebig discovered, gave a different result. The aqueous solution gave with nitrate of silver a precipitate of *pure white;* the ash, therefore, contains a bibasic alkaline phosphate, and when it was acted on by nitric acid and again ignited, the soluble portion still precipitated nitrate of silver *only* white, although an additional quantity of alkali was thus added to the phosphate originally present. From this it follows, that the juice of the flesh of fowl must contain a certain, though small quantity of an alkaline monophosphate, since, otherwise, after the action of nitric acid on the ashes, a certain quantity of an alkaline tribasic phosphate must have been produced, and thereby a yellow precipitate must have been formed, to a corresponding extent, with the nitrate of silver.

770. *Examination of the hydrochloric solution.*—Add ammonia very slightly in excess, then add acetic acid in excess; if a white precipitate remains undissolved by the acetic acid it is due to the presence of phosphate of sesquioxide of iron; filter a small portion of the liquid, and test for peroxide of iron with ferrocyanide of potassium; if there is iron present in the filtrate it shows there is more sesquioxide of iron than corresponds to the phosphoric acid; if there is no iron present in the filtrate add some sesquichloride of iron to the unfiltered portion until the fluid looks reddish; in either case, that is, whether the iron is in excess or iron is added in excess, boil the unfiltered portion until it is all removed; when this is accomplished filter hot, and mix the filtrate after the addition of ammonia and sulphide of ammonium, and allow it to stand in a corked flask for some time; if a precipitate should form, test it for manganese; filter and examine the filtrate for lime and magnesia in the usual way.

771. *Examination of the residue insoluble in hydrochloric acid.*—The residue insoluble in hydrochloric acid contains—

1. The silicic acid which has separated on treating with hydrochloric acid.

2. Those ingredients of the ash which are insoluble in hydrochloric acid. These are, in most cases, ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stalk of cereals and others abounding in silicic acid that are not completely decomposed by hydrochloric acid.

772. It is rarely necessary in an examination which is not going to be extended beyond a qualitative analysis to examine this residue further; but in cases where it is desirable, the analysis for all the bases, with the exception of the alkalies, must be conducted according to par. 721, and for the alkalies according to par. 725.

ANIMAL CHEMISTRY.

773. We shall first give in groups, as far as it is possible, the chief organic compounds met with in the animal organism, with their properties and reactions; and afterwards a method for the proximate analysis of mixed animal substances (946), and lastly a method for the analysis of urine (966). Before commencing the proximate analysis the student is recommended to go through the chief groups, performing all the experiments given.

THE ALBUMINOID OR PROTEIC GROUP.

ALBUMEN, FIBRIN, CASEIN, GLOBULIN, VITELLIN.

774. *Properties of the Group.*[*]—The members composing this group are met with in the vegetable as well as the animal kingdom; they are uncrystallizable, and in their pure state they are tasteless and inodorous. They exist in the living organism both in the soluble and insoluble state; they are present in the soluble form in the fluids, and in the insoluble form in the solid parts of plants and animals. When freshly precipitated from their solutions, and whilst still moist they are usually whitish in colour, and appear as a flocculent precipitate or in small clots; when dried and unpowdered they are tough and gelatinous.

775. These substances when dried and if not exposed to moist air, will keep for any length of time unchanged. But if moist or exposed to moisture they speedily decompose and putrefy, and this is one of their most striking characters; they are *ferments* in their decomposing or putrefying state, yeast,

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[*] Globulin and vitellin are not included in the remarks on the properties of the group; these observations only strictly apply to albumen, fibrin, and casein.

wine-lees, diastase, synaptase, pepsin, for instance, are albuminoids in a peculiar state of decomposition.

776. If these bodies are heated in close vessels (subjected to dry distillation), they first swell up and fuse, then blacken, and emit a large quantity of fœtid empyreumatic products among which ammonia and sulphuretted hydrogen are always present; and they leave in the retort a porous, brilliant, carbonaceous mass. When burned they leave a notable amount of ash; this varies in quantity in different cases, but it always contains phosphate of lime.

777. They all yield the same products when treated with oxidizing agents, such as peroxide of manganese, or bichromate of potash and sulphuric acid; the volatile products are the only class which have been fully examined, the following are the volatile substances which have been identified:

Formic acid.
Acetic acid.
Propionic acid.
Butyric acid.
Valeric acid.
Caproic acid.
Acetic aldehyd.
Propionic aldehyd.
Butyric aldehyd.
Benzoic acid.
Hydride of benzoyl.
Hydrocyanic acid.
Valeronitrile.

778. The albuminoids are insoluble in alcohol and ether and are even precipitated from their aqueous solutions on the addition of alcohol to the liquid, the precipitate is generally insoluble in water after its precipitation by alcohol.

779. "These substances either in their soluble, or insoluble state, are readily dissolved by the aid of a gentle heat in a solution of potash or soda, the addition of an acid to their alkaline solution so obtained causes the separation of a grayish flocculent precipitate, termed by Mulder protein, while a slight odour of sulphuretted hydrogen is emitted, and a small quantity of phosphoric acid is also found in the solution. This precipitation is best effected by means of acetic acid, since the mineral acids are obstinately retained by the flocculi."
—*Miller*.

780. In concentrated sulphuric acid these substances dissolve with a brownish-red colour.

781. Concentrated nitric acid produces in solutions of these substances a precipitate of a bright orange colour, which gradually dissolves in the acid with effervescence; nitric acid added to the substances in the insoluble state colours them yellow and finally dissolves them. Mulder considers the yellow colour to be due to the formation of a distinct compound which he has called *xanthoproteic* acid.

782. When to a solution of these substances concentrated hydrochloric acid is added, and the solution is gently warmed, a white precipitate is first produced, which gradually dissolves, forming, if in contact with atmospheric air, a blue or violet-coloured liquid. The reactions with nitric acid and hydrochloric acid are very characteristic of the albuminoids.

783. Most acids produce a precipitate in solutions of these substances, but when they are added in excess redissolve the precipitate; when these acid solutions are diluted with a moderate quantity of water, a precipitate is formed which disappears on the further addition of water.

784. Monophosphoric acid (metaphosphoric acid), produces a precipitate in solutions of these substances, but an excess of the acid does not redissolve the precipitate.

785. Tannic acid produces a precipitate in solutions of these substances, and an excess of the acid does not redissolve the precipitate.

786. The acid solutions, but not the aqueous solutions of the albuminoids give a precipitate with the ferrocyanide and ferricyanide of potassium; the next group of substances gives no precipitate with these reagents.

787. If a solution of mercury, prepared by dissolving two parts of mercury in four parts of nitric acid, of sp. gr. 1·40 be added to a solution of the albuminoids, or, if in the solid state, they are moistened with the mercury solution, and the moistened solid or the fluid is then heated to a temperature from 140 to 212° F., an intense red colour is produced, which is not destroyed by boiling with water, nor by exposure

to the air; the colour is so intense that it may be perceived on adding the mercurial solution to a liquid containing not more than 1 part of albumen in 100,000 parts of water. The mercury solution gives a similar coloration with the members of the next group.

788. The aqueous solution of these bodies is precipitated by salts of copper, of lead, and of mercury, the precipitate generally contains the acid and base of the salt employed in addition to the albuminoid.

789. If a solution of these substances be mixed with a solution of sulphate of copper, and then a large excess of caustic potash be added, the greenish precipitate first formed is redissolved, and the liquid acquires a purple tint of great intensity and magnificence. The same reaction takes place with the next group of substances, and probably with any of the more complex nitrogenous substances.

790. In the living organism, fibrin, casein, and albumen are converted into one another, for example, the casein in milk, when this substance is used as food, must be converted in the animal economy into albumen and fibrine, and the two latter albuminoids must be converted into casein in the formation of milk. As the albuminoids have the same or nearly the same constitution, as shown by the following analyses, their conversion into one another can be easily accounted for. In the subjoined analyses the ash has been deducted previous to calculating the composition in 100 parts:—

	Albumen.	Fibrin.	Casein.
Carbon	53·5	52·7	53·83
Hydrogen	7·0	6·9	7·15
Oxygen	22·0	23·5	22·52
Nitrogen	15·5	15·4	15·65
Sulphur	1·6	1·2	0·85
Phosphorus . . .	0·4	0·3	
	100·0	100·0	100·00

791. With the exception of casein not containing phosphorus as an organic constituent, the analyses of these substances do not differ from one another more than the analyses of the same substance would do if it were obtained from different sources. The presence of phosphorus as an organic constituent in albumen and fibrin although given in the analyses, has not yet been well established; and therefore with regard to this substance it may hereafter be found that casein does not differ from the other two in composition.

792. The determination of the *rational formula* of bodies like the albuminoids is beset with difficulties; the difficulties are so great with regard to these substances that they have not yet been overcome, and consequently their rational formula has not been determined. Different views have, however, been put forward to explain the relation between them, for, from their great similarity in composition and properties, there can be no doubt but that they are very closely related. The first view we shall notice is that of Mulder, as, although now abandoned, it is constantly referred to in works on the science; this view when first promulgated by the author was almost universally accepted by chemists, but they have long regarded it as erroneous.

793. Mulder considered that the flocculent precipitate obtained by adding an acid to an alkaline solution of the albuminoids was free from sulphur and phosphorus, and that this nitrogenized precipitate has identically the same composition, whether obtained from fibrin, albumen, or casein. This substance, which he called protein, he regarded as the fundamental principle of each of the albuminoids, and that albumen, fibrin, and casein were produced by the combination of different quantities of sulphur and phosphorus with protein; admitting this view of the construction of these bodies, it was easy to account for their conversion into one another, for the elimination or combination of small quantities of sulphur and phosphorus was all that was required to effect the change.

794. The so-called protein substance, Liebig has shown, is never obtained free from sulphur, that it always contains a

small but variable quantity of this element; he considers that the precipitate is not a new and distinct substance, but that it is the original body slightly modified by the action of the potash.

795. "Gerhardt was of opinion that all the albuminoids are identical, not only in composition, but in chemical constitution, and that they differ from one another only in molecular arrangement, and by the nature of the mineral substances with which they are associated; in fact, that they contain a common proximate element, which, like many other organic compounds, is capable of existing in a soluble and an insoluble modification. Designating this common element by the name albumin, he supposed that white of egg and serum consist of acid albuminate of sodium, which is separated by heat into free albumin and neutral albuminate of sodium, the latter remaining dissolved; that casein, which is soluble and non-coagulated by heat, consists of neutral albuminate of potassium, from which the organic compound may be precipitated by neutralizing the alkali with an acid; and that fibrin is albumin in the insoluble state, more or less mixed with earthy phosphates. This view is in accordance with the fact that fibrin and casein may be dissolved in neutral potash salts (better with addition of a little caustic alkali), forming a liquid which coagulates by heat, and deflects the plane of polarization of a luminous ray to the left, like albumin; and that fibrin and albumin, dissolved in a certain quantity of caustic alkali, exhibit the characters of soluble casein. Nevertheless, it is possible to obtain the albuminoids in some cases wholly, in others very nearly, free from mineral matters, and nevertheless exhibiting their distinguishing characteristics.

796. "Strecker supposes the albuminoids to be composed of a great number of radicles (a supposition in accordance with the variety of their products of decomposition), that the greater number of these radicles are the same in all, hence their great similarity; but that each contains one or more such radicles peculiar to itself. Thus, when casein is converted in the animal body into albumen and fibrin, it may take the radicles required for that transformation from the other constituents

of the milk, viz., the fat and the sugar."—*Watts' 'Dictionary of Chemistry.'*

ALBUMEN.

797. *Properties of soluble Albumen.*—An aqueous solution of albumen is a tasteless, odourless, and colourless, but somewhat glairy liquid. It exerts a left-handed rotatory action upon a ray of polarized light. It is adhesive, and when spread on paper it forms when dried a varnished surface. Soluble albumen in the solid state is translucent and of a pale yellow colour; it is tasteless and inodourless; it swells in water assuming a gelatinous appearance: it does not dissolve freely in pure, but very readily in water containing any alkaline salt.

798. If its aqueous solutions are evaporated to dryness at a temperature *not exceeding* 120° F., the solid albumen thus obtained will dissolve, although slowly, in water; its solution is greatly promoted by the addition of chloride of sodium or any salt of the alkalies; a varying quantity of the albumen always becomes converted by the evaporation into the insoluble state.

799. If an aqueous solution of albumen is heated to about 150° F. it becomes opalescent, and at 170° F. it becomes entirely converted into the insoluble form. This conversion of the soluble into the insoluble form by heat, is the most characteristic property of albumen. The reason of the conversion is not known. Dumas thinks that it is probably a simple isomeric modification analogous to the conversion of cyanic into cyanuric acid.

800. *Action of alcohol, ether, &c. on soluble Albumen.*—*Strong* alcohol precipitates albumen from its solutions and after its precipitation by this liquid, it will not redissolve in water. If the alcohol is rendered slightly alkaline by potash, it causes no precipitate in solutions of albumen. *Weak* alcohol also precipitates albumen from its solutions, but the precipitate redissolves completely in water.

801.* *Ether*, if free from alcohol, only gelatinizes the albumen, it does not coagulate it.

802. *Kreasote* and *aniline* precipitate and coagulate it immediately.

803. *Rennet* does not precipitate it from its solutions. The *volatile* and *fixed* oils have no action upon it.

804. *Action of acids on soluble Albumen.*—The action of concentrated sulphuric, hydrochloric and nitric acids on albumen, and the other albuminoids has already been noticed (780, 781, 782).

805. Dilute sulphuric acid produces no precipitate in solutions of albumen until the liquid is boiled.

806. Dilute hydrochloric acid precipitates it at first, but afterwards redissolves it; this solution becomes milky on the addition of a little water; but if more water is added it becomes perfectly clear again.

807. Dilute nitric acid precipitates it readily and completely, and does not redissolve it; the precipitate is soluble in a large quantity of water. Dilute nitric acid is frequently employed as a test for the presence of albumen.

808. Monobasic phosphoric acid (metaphosphoric acid) precipitates it immediately and completely. The tribasic and bibasic phosphoric acids do not precipitate it.

809. The organic acids, tannic acid excepted, (785), cause no precipitate in moderately concentrated solutions of albumen; its solutions, in the presence of organic acids do not coagulate by heat, but a pellicle gradually forms over the surface during evaporation.

810. Serum or white of egg mixed with a certain quantity of *common salt*, or other salt of an alkali-metal forms a liquid precipitable by phosphoric, acetic, tartaric, oxalic, lactic acid, &c.; conversely, a solution of albumen, (or other albuminoidal substance) in acetic acid is precipitated by the salts of the alkali-metals. The precipitation is greatly facilitated by heat, and likewise takes place with greater facility as the proportion of salt added is greater. The precipitate dissolves in pure water, with greater facility in proportion as less heat has been

applied in producing it; the solution is not coagulated by heat. It is soluble also in acetic acid, phosphoric acid, and even in alcohol, provided it has not been altered by desiccation, or by contact with the air. The aqueous solution is precipitated by certain salts, ferrocyanide of potassium for example.

811. When a small quantity of acetic acid is added to white of egg or serum, so as just to saturate the alkali, and the liquid is then largely diluted with water, flocks of albumen are deposited after a while. If the supernatant liquid be then decanted, and the precipitate treated with a small quantity of solution of nitre or common salt, it immediately dissolves, and the solution is coagulated on boiling.

812. *Dried soluble* albumen suspended in acetic, tartaric, or citric acid, swells up and is converted into coagulated albumen, which may be completely free from acid by washing.

813. Chlorine and bromine precipitate albumen from its solutions.

814. *Action of salts on soluble Albumen.*—"The greater number of the metallic salts, as iron, copper, lead, mercury, silver, antimony, aluminum, precipitate albumen; the precipitate consisting either of a combination of a basic salt with albumen, or a mixture of two compounds, one of which consists of the acid of the salt and albumen, and the other of the base of the salt and albumen. The albumen generally passes into the insoluble state in these combinations; the precipitate is generally soluble in an excess of serum or white of egg, and in some cases in the salt which produces it. Albumen, owing to its forming precipitates with them, is a valuable antidote in cases of poisoning by metallic salts.

815. " Corrosive sublimate is a delicate test of the presence of albumen, a liquid containing only a two-thousandth part of solid albumen is precipitated by it. The white precipitate formed is an insoluble compound of the salt with the organic substance; albumen, it is well known, is the antidote which is employed in this form of poisoning."

816. *The action of the alkalies and alkaline carbonates on soluble Albumen.*—The presence of an alkali, or an alkaline

carbonate in a liquid containing albumen, greatly modifies the reactions of that substance; if the alkali is present in considerable quantities the solution does not coagulate by heat; but if it be evaporated, a pellicle forms over the surface similar in appearance to that produced upon a solution of casein by heat. Also, if to an alkaline solution of albumen, acetic, tartaric, or tribasic phosphoric acid, acids which in neutral or slightly alkaline solutions of albumen, cause no precipitate, is added, a precipitate is produced which readily dissolves in an excess of the acid. These characters resemble those of casein and some chemists have supposed that casein is simply an albuminate of potash.

817. If alcohol be added to an alkaline solution of albumen, it causes, as we have already noticed, no precipitate.

818. If a concentrated solution of potash be added to a concentrated solution of albumen, albuminate of potash in the form of a gelatinous mass is produced; by washing the precipitate with cold water the greater part of the alkali can be removed, 5·4 per cent. of the alkali only remaining. If the gelatinous mass be washed with alcohol and then with water, it is insoluble in boiling alcohol and boiling water; but if it be washed with cold water, it is soluble in boiling water and boiling alcohol.

819. *Properties of insoluble Albumen.*—Insoluble albumen when moist appears as a white opaque elastic solid, it turns blue litmus *red.* When dried it is of a pale yellow colour, and becomes brittle and translucent like horn. If the dried substance be immersed in water it absorbs about four or five times its weight of water and regains the consistence of the undried substance. When coagulated albumen is boiled in water for about sixty hours in open vessels it undergoes gradual decomposition, and a soluble compound is obtained which according to Mulder is teroxide of protein and ammonia. If heated to 300° F. with a small quantity of water in a sealed tube the albumen is redissolved, and furnishes a liquid which does not coagulate by heat, but which, when acidulated with acetic acid, gives a precipitate with ferrocyanide of potassium.

820. *On the varieties of Albumen.*—"The properties of albumen vary in some degree with the source from which it is derived. The differences may in some cases be attributed to the presence of different mineral substances, but in others they are of such a nature as rather to point to the existence of different modifications of albumen. Thus Frémy and Valenciennes have found that the albumen of the eggs of certain tribes of birds exhibits peculiar modifications. That from the eggs of different species of gallinaceous birds always exhibits the characters above described; but the eggs of swimming and wading birds yield an albumen which, when diluted with three measures of water, is not coagulated by heat, but is precipitated by nitric acid; and the albumen from the eggs of predacious birds and some kinds of perching and climbing birds is neither coagulated by heat nor precipitated by nitric acid. The composition was, however, found to be the same in all cases.

821. "Blood-albumen exhibits the same reactions as that from white of egg, excepting that the latter when boiled gives up part of its sulphur in the form of sulphuretted hydrogen, which blood-albumen does not; nevertheless coagulated white of egg appears to contain more sulphur than blood-albumen."
—*Watts' 'Dictionary of Chemistry.'*

FIBRIN.

822. Fibrin exists only in solution in the living plant or animal, for as soon as the solution is removed from the living organism it immediately begins to coagulate; this character distinguishes it from other analogous substances. The coagulation of the fibrin is prevented if the blood or other liquid containing the fibrin, at the moment it leaves the living organism, is mixed with solutions of certain salts, such as carbonate or nitrate of potash, acetate or sulphate of soda, and chloride of sodium.

823. *Properties of Fibrin.*—Undried coagulated fibrin appears in the form of long, white, elastic filaments, but when dried it forms a horny yellowish or grey solid. Both in the dried and undried state it is tasteless and insoluble both in hot and cold water, in alcohol, ether, &c. When long boiled, however, with water, it is, like albumen, gradually dissolved; by the exposure to heat and moisture it has evidently undergone decomposition, for the solution contains traces of ammonia. If undried fibrin is covered with water, it becomes in a few days viscid and acquires the odour of old cheese.

824. *Action of acids on Fibrin.*—The action of concentrated hydrochloric, sulphuric, and nitric acids on fibrin and the other albuminoids has already been noticed (780, 781, 782).

825. When fibrin is immersed for about twelve hours in water slightly acidulated with hydrochloric acid, it becomes gelatinous, and when this jelly is triturated with water, it yields a solution which coagulates by heat, is precipitated by ferrocyanide of potassium, and affords a precipitate on the addition of hydrochloric acid, not soluble except in an excess of this acid. According to Dumas and Cahours, water containing a millionth part of hydrochloric or hydrobromic acid gelatinizes fibrin, and if a few drops of gastric juice (pepsine) be then added, it is entirely dissolved in a couple of hours at a temperature of 96° to 100° F. Rennet produces the same effect.

826. Monobasic phosphoric acid (metaphosphoric acid) does not dissolve fibrin. Tribasic phosphoric acid converts it into a gelatinous mass which is soluble in water, the fibrin is not precipitated from this solution on the further addition of the acid.

827. Concentrated acetic acid converts it into a gelatinous mass which is soluble in pure water. Sulphuric acid and metaphosphoric acid precipitate it from this solution, the precipitate consisting of a compound of fibrin and the precipitating acid. Ferrocyanide of potassium precipitates fibrin from its acetic solution. Alkalies also precipitate it, but the precipitate is redissolved by an excess of the alkali. According

to Dumas the fibrin of young animals is more easily acted on by acetic acid than that of old ones, so that there is in this respect a material difference between the fibrin of veal and of beef.

828. *Action of the alkalies on Fibrin.*—Weak solutions of potash and soda dissolve fibrin, ammonia exerts the same influence, but less rapidly; acetic and phosphoric acids and also the metallic salts precipitate fibrin, as they do albumen, from its alkaline solutions. Indeed an alkaline solution of fibrin resembles an alkaline solution of albumen in most of its characters.

CASEIN.

829. *Properties of soluble Casein.*—Although this substance is met with in a state of solution in milk it is doubtful whether this substance has a soluble form; it is considered that its soluble state in milk is due to a small quantity of free alkali; casein in solution does not coagulate by heat, the solution merely becomes covered with a film which is formed as often as it is removed. The casein of milk when obtained in the solid state does not redissolve completely in water.

830. *Action of alcohol, rennet, &c., on soluble Casein.*—Casein in solution is coagulated by alcohol, a portion at the same time entering into solution; a larger quantity is dissolved by boiling alcohol. The coagulum produced by absolute alcohol is insoluble in pure water; but the portion dissolved by alcohol is, after the removal of the alcohol, found to be still soluble in water.

831. Rennet (the inner membrane of the fourth stomach of the calf, salted and dried), or an infusion of it prepared at a low temperature, coagulates casein completely; this is the most remarkable and important mode of coagulating casein.

832. *Action of acids on Casein.*—The action of concentrated hydrochloric, sulphuric, and nitric acids on fibrin and the other albuminoids has already been noticed (780, 781, 782).

833. Casein is precipitated from its solutions by all acids with the exception of carbonic acid, the precipitate redissolves in an excess of the acid; from its solution in acetic acid the mineral acids and ferrocyanide of potassium precipitate it.

834. The coagulation of milk is due to the lactic acid, which is formed from lactine, neutralizing the alkali which renders the casein soluble, and thus causing that substance to pass into its insoluble state.

835. *Action of bases and of salts.*—"Coagulated casein is readily dissolved by solutions of the alkalies and of the alkaline carbonates; and if the solution be very feebly alkaline, the alkaline reaction may be completely neutralized by the casein. Solutions of common salt, of nitrate of potash, and of muriate of ammonia, likewise dissolve casein with facility, and these solutions, when evaporated by the aid of heat, become covered with an insoluble pellicle. Casein also unites with the alkaline earths and forms compounds which are insoluble in water. If a piece of poor cheese, which consists principally of casein, be reduced to a paste with water and mixed with slaked lime, it produces a tenacious lute, which sets very hard, and may be used for cementing pieces of broken earthenware. In consequence of the tendency to the formation of these insoluble compounds, a solution of casein is precipitated by salts of lime or by sulphate of magnesia, upon the application of heat to the mixture; this reaction is very characteristic of casein. Most of the metallic salts, such for instance as acetate and subacetate of lead, sulphate of copper, subnitrate of mercury, and corrosive sublimate, occasion precipitates in the cold with solutions of casein."—*Miller.*

GLOBULIN.

836. Globulin occurs in the cells of the crystalline lens in a very concentrated solution. It is one of the principal con-

stituents of the blood, since, with hæmatin, it forms the viscid fluid contents of the blood-corpuscles. It has not yet been found in any other parts of the animal body.

837. Globulin is very similar in its properties generally to albumen and vitellin, but it is distinguished from them by "its solutions not becoming opalescent at a lower temperature than 163·5° F.; at 181·5° F. it assumes a milky turbidity, and at 199·5° F. separates as a globular mass (if it be still mixed with hæmatin) or as a milky coagulum which never becomes clear on filtration, and from which neither small quantities of acetic acid or ammonia separate flakes capable of being removed by filtration; it is only when neutral alkaline salts are added, and the solution is then boiled, that the fluid becomes perfectly clear and flakes and small clots are deposited. The following reaction is very characteristic of globulin; its solution is not precipitated either by acetic acid or by ammonia, but it becomes strongly turbid when the fluid treated with acetic acid is neutralized with ammonia, or conversely when after the addition of ammonia it is neutralized with acetic acid. No other *soluble* albuminoid is precipitated both from its acid and its alkaline solution by neutralization, although almost all the *insoluble* albuminoids possess this property—a circumstance which affords a proof that globulin is reduced to the coagulated state both by an excess of alkali and by an excess of acid."—*Lehmann.*

VITELLIN.

838. This is the albuminous body of the yelk of egg; it is so similar to albumen that, until recently, it has been confounded with the albumen of the white of egg, like the latter, it exists both in a *soluble* and in an *insoluble modification;* the former is not precipitated from its aqueous solutions by organic acids or by ordinary phosphoric acid, but is thrown down by sulphuric and hydrochloric acids; at 140° F. its solution begins to become opalescent, and at from 163·5° F. to 169° F.

there is a deposition of larger or smaller flakes. It is only distinguished from soluble albumen by the circumstances that (without the addition of acetic acid or of salts) when heated, it forms flakes and clots, that it is not precipitated by the salts of oxide of lead or of copper, and that it is thrown down by ether. (*Lehmann.*)

839. *Recapitulation and remarks.*—This group of substances is distinguished from a large number of substances by *containing nitrogen;* the method for testing organic substances for this element is given at par. 751.

840. The substances forming this group are distinguished from a large number of organic substances containing nitrogen, by containing sulphur; the method for testing organic substances for this element is given at pars. 752 to 756. They are distinguished from the next group of substances by being precipitated from their acid solutions by ferrocyanide of potassium.

841. Albumen is usually distinguished and separated from the other members of the group, by warming the fluid and coagulating; if the solution is alkaline it is necessary to *neutralize* it with acetic acid, care being taken not to add the acid in excess before warming the liquid; if the solution is very acid it ought to be neutralized, or the acid or alkaline liquid, instead of being neutralized, is treated with a strong saturated solution of chloride of ammonium; when chloride of ammonium is employed, the solution requires a longer boiling in order to completely precipitate the albumen from the fluid than if it had been neutralized.

842. Fibrin is distinguished from the other albuminoids by the property which it possesses of coagulating spontaneously; it can exist only in the soluble form in the living plant or animal.

843. Casein in the absence of, or after the removal of albumen, may be detected by adding to the solution sulphate of magnesia, or chloride of calcium, and then warming the solution, if casein is present a precipitate will be formed. But the test which distinguishes it from the other albuminoids is rennet; but to render this test reliable, the rennet must be tolerably

fresh, or at least free from all putridity; the mixture should be digested for a period not exceeding two hours, and at the temperature of 104° Fahr.

844. The characteristic tests for globulin and vitellin are described at pars. 837 and 838.

GELATIGENOUS GROUP.

Gelatin. Chondrin.*

845. *Properties of the group.*—Under the term gelatin we include the organic tissue of bone, cartilage, sinew, ligament, skin, cellular tissue, and serous membrane; all these substances dissolve by long-continued boiling in water, and the solution on cooling assumes a consistent gelatinous mass. It is represented in various degrees of purity by glue, size, and isinglass. Gelatin does not exist *as gelatin* in the animal tissues, but is formed from them by the action of boiling water. Müller has shown that there are two (if not three) distinct forms of gelatin. To that which is obtained from the permanent cartilages, the cornea, fungous bones, &c., the term *chondrin* is given, while *glutin* includes those forms of gelatin which are obtained from skin, serous membrane, hoof, bone, tendon, fibrous and spongy cartilage, cartilage of bone, &c.

846. The gelatigenous substances have hitherto been found only in animals. They contain a smaller amount of carbon and sulphur and a larger amount of nitrogen than the members of the albuminoid group, as will be seen on comparing the following table with the one given at page 265.

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* There are two other bodies known—Fibroin and Chitin—which belong to this group, but we have omitted them on account of their unimportance.

	Chondrin.	Gelatin.
Carbon	49·97	50·40
Hydrogen . . .	6·63	6·64
Nitrogen . . .	14·44	18·34
Sulphur . . .	0·38	24·62
Oxygen	28·58	
	100·00	100·00

847. The members of this group yield the same products as the members of the preceding group when treated with oxidizing agents, such as peroxide of manganese, or bichromate of potash and sulphuric acid (777).

848. These substances also give the same reaction as the members of the previous group with nitrate of mercury. (See 787.)

849. The members of this group are especially distinguished by the following properties; they swell and become very translucent in cold water; they dissolve in hot water; on cooling they separate as translucent lubricous masses, and are precipitated from the most dilute solutions by chlorine, tannic acid and most of the salts of the earths and metals.

GELATIN (Glutin).

850. Gelatin in a state of purity is a colourless transparent solid, which is hard, horny, and brittle; it is devoid of taste and smell, and has no action on vegetable colours. It is insoluble in alcohol and ether; it is insoluble in *cold* water, but softens and swells up in it; in *warm* water it dissolves, but the liquid as it cools becomes converted into jelly, gelatinizes, hence the name gelatine; 1 part of pure gelatine dissolved in about 80 parts of water, is sufficient to cause the liquid to gelatinize when it cools. If a solution of gelatine is boiled

for a length of time, it does not gelatinize on cooling; the gelatine appears to be converted by the boiling into an isomeric modification which does not possess the property of gelatinizing.

851. Lime and phosphate of lime are much more soluble in a solution of gelatin than in cold water. Common glue always contains a large quantity of phosphate of lime, and this substance is considered by Mulder to be an essential constituent of gelatine; and it may be observed that chemical compounds of gelatine and phosphate of lime can be prepared.

852. Moist gelatin exposed to the air rapidly putrefies; the liquid at first becomes highly acid, but afterwards gives off a large quantity of ammonia. This property of first becoming acid is characteristic of gelatine.

853. *Action of acids on Gelatine.*—Gelatin is soluble in all the dilute acids with the exception of tannic acid; and it is not precipitated from its solutions by any of the acids except tannic acid.

854. It is dissolved by concentrated sulphuric acid in the cold without change of colour. The solution diluted with water, and boiled, yields leucine, glycocine (sugar of gelatine) and some other products.

855. When gelatine is boiled with concentrated nitric acid, it becomes gradually converted into oxalic acid, saccharic acid, and two substances resembling suet and tannic acid. When a solution of gelatine in dilute nitric acid is evaporated, nitrous gas is evolved, and the residue deflagrates just before dryness.

856. Tannic acid is a most delicate test of the presence of gelatine; when it is added to a solution of 1 part of gelatine in 5,000 of water, a cloud is evident, and on adding the acid to a strong solution, a dense light-coloured precipitate is produced, (tanno-gelatine) which is insoluble in water, alcohol, and ether, but soluble in a warm solution of potash. The composition of the precipitate does not appear to be constant. Tanno-gelatin is identical with *leather*.

857. *Action of chlorine.*—If chlorine gas is passed through

a solution of gelatin, a white pellicle forms round each bubble of the gas, and finally the whole of the gelatine is precipitated in the form of white elastic flakes or filaments. The precipitate is tasteless, slightly acid, imputrescible, insoluble in water and alcohol, but soluble in acids; its composition is not known. No similar substance is obtained by substituting bromine or iodine for chlorine.

858. *Action of the alkalies.*—A pure solution of gelatin is not precipitated by dilute solutions of the alkalies. When the gelatin solution is boiled with a concentrated solution of potash it is decomposed into leucine, glycocine and other products. The same change takes place when gelatine is carefully fused with solid potash.

859. The solubility of lime and its phosphate in solutions of gelatin has already been noticed.

860. *Action of salts.*—" Salts of lead, of copper, of alumina, and of iron, do not produce any precipitates in solutions of gelatine, but if a solution of potash be added to the mixture of gelatine with alum, or with persulphate of iron, the subsulphate of alumina or iron, which is formed carries down a large proportion of gelatin."

861. Protochloride of mercury precipitates gelatin from its aqueous solution.

CHONDRIN.

862. Chondrin is transparent, horny, and glistening, it softens to a jelly in cold water, and in warm water it dissolves, but the liquid as it cools gelatinizes. It is insoluble in alcohol and ether. If a solution of chondrin be boiled for a length of time it does not gelatinize on cooling.

863. *Action of acids.*—" Nearly all acids, even organic acids, precipitate chondrin from its aqueous solution. The precipitate formed by hydrochloric, sulphuric nitric, phosphoric, phosphorous, chloric, or iodic acid, redissolves easily in excess of the acid; that formed by sulphurous, pyrophosphoric, hydro-

fluoric, carbonic, arsenic, acetic, tartaric, oxalic, citric, lactic, succinic or tannic acid does not redissolve in excess of the acid employed."

864. "Strong sulphuric acid dissolves chondrin, forming a syrupy liquid, which, when diluted with water and boiled, yields leucine without glycocine. Sulphurous acid slowly decomposes chondrin. Nitric acid, by prolonged action, converts it into xanthoproteic acid.

865. *Action of chlorine.*—"The aqueous solution of chondrin treated with chlorine yields a precipitate.

866. *Action of salts.*—"Alum, sulphate of alumina, acetate and subacetate of lead, sulphate of copper, sulphates of the protoxide and of the peroxide of iron, sesquichloride of iron, nitrate of suboxide and of the protoxide of mercury, produce copious precipitates in a solution of chondrin, soluble for the most part in excess of the reagent. The precipitates formed by acetic acid, alum and sulphate of alumina, dissolve completely on adding a sufficient quantity of acetate of potash, acetate of soda, or of common salt. The precipitate formed by sulphate of the sesquioxide of iron redissolves on heating the liquid.

867. "Protochloride of mercury does not precipitate a solution of chondrin; sometimes a slight turbidity is produced, owing apparently to the presence of a little gelatine."

868. *Recapitulation and remarks.*—This group of substances is distinguished from a large number of organic substances by *containing nitrogen.* They are distinguished from the members of the preceding group by ferrocyanide of potassium producing no precipitate in their solutions. And their peculiar behaviour with water at once distinguishes them from all other substances.

869. Gelatin is distinguished from chondrin by giving a precipitate with protochloride of mercury.

870. Chondrin is distinguished from gelatin by being coagulated by the vegetable acids such as acetic acid, as well as by alum, and by the neutral and basic acetates of lead.

SUGARS.

MILK-SUGAR, GRAPE-SUGAR (Glucose), INOSITE.

871. As milk-sugar, glucose, and inosite, are the chief varieties of sugar met with in the animal kingdom, they are the only sugars we shall notice in this part of the work.

872. The sugars are all soluble in both cold and warm water, but they are more soluble in hot water than cold. They all possess a sweet taste; but there are great differences in the relative sweetness of the different varieties.

Sugar of milk (Lactin, Lactose) $C_{24}H_{19}O_{19}+5HO$.

873. This variety of sugar is an animal product, it is found only in the milk of the mammalia, and is the substance which gives the sweet taste to fresh milk. It forms white, translucent four-sided prisms, of great hardness. It is soluble in about six parts of cold, and two parts of boiling water; it does not form a syrup, and has only a feeble sweet taste. It is insoluble in alcohol and ether. Its aqueous solution produces right-handed rotation of a ray of polarized light.

874. It is converted into glucose when boiled with dilute acids. Nitric acid converts it into mucic acid, with a little oxalic acid; it differs from the other sugars, and resembles the gums in furnishing these acids by the action of nitric acid upon it.

875. It becomes gradually converted in milk, from the influence of the caseous matter, into lactic acid, thus:—

$$C_{24}H_{24}O_{24} = 4(HO, C_6H_5O_5).$$

876. Milk-sugar reacts with sulphate of copper and potash, exactly in the same manner as glucose (822).

Grape or Starch Sugar, *Glucose*, $C_{12}H_{12}O_{12}+2HO$.

877. Grape-sugar abounds in grapes, figs, plums, and othe fruits; it is also formed from starch, cane-sugar, and woody fibre, by processes which will be described under Vegetable

Chemistry. It is also a morbid constituent of the urine in the disease called *diabetes*, its appearance in the urine is the most characteristic feature of the disease.

878. "Glucose crystallizes with difficulty in warty concretions, composed of hard transparent cubes. It forms with common salt a compound that crystallizes with facility, which is a distinctive character of this variety of saccharine matter.

879. "Glucose is distinguished from cane-sugar by several characters; it is considerably less soluble in water than cane sugar, though it is more readily taken up by alcohol, and crystallizes from a hot solution of alcohol containing not more than 5 per cent. of water in anhydrous prisms ($C_{12}H_{12}O_{12}$). It requires nearly two and a half parts of glucose to produce the same sweetening effect as is produced by one part of cane-sugar. The action of sulphuric acid upon grape-sugar is quite different from its action upon cane-sugar, as, instead of charring and destroying it as it does with cane-sugar, it forms with it a definite compound acid, the solution of which is pale yellow; this acid has been termed sulphosaccharic acid."

880. Grape-sugar is resolved in contact with yeast or other ferments into alcohol, carbonic acid and water: thus—

$$C_{12}H_{14}O_{14} = 2(C_4H_5O, HO) + 4CO_2 + 2HO.$$

881. When a solution of grape-sugar is heated with a solution of one of the fixed alkalies it is rapidly decomposed, which is evidenced by the fact that the liquid darkens in colour and finally becomes nearly black. This action of the fixed alkalies on grape-sugar has been proposed as a test for sugar in urine; it is called Moore's test and is employed as follows:—To the suspected urine, an equal bulk of the ordinary solution of caustic potash is to be added and the whole boiled gently for about five minutes; a deep orange-brown or black colour will be produced if sugar is present. This test ought only to be employed as a confirmatory test, as in many cases it might prove a very fallacious test.

882. The dark brown substance (melassic acid), which is produced when an alkaline solution of sugar is heated, has a

very powerful affinity for oxygen, it speedily reduces black oxide of copper to the red oxide (suboxide) when a salt of copper is added to the alkaline solution of sugar. On this property is founded the most valuable chemical test for sugar which we possess; this test is known as Trommer's test. The simplest plan of employing this test is to add a solution of caustic potash in tolerable excess,* if a precipitate is produced, as is frequently the case in urine, filter and to the filtrate (in a test-tube) add a few drops of a *very dilute* solution of sulphate of copper.† If sugar is present, the precipitate which first forms is redissolved on shaking, and the fluid becomes of a clear blue colour. This blue solution is then heated to boiling, whereon a yellow cloud (hydrated suboxide of copper) forms, which is speedily converted into red anhydrous suboxide which precipitates.

883. When testing urine for sugar by this method the mixture of urine and potash should not be warmed before the addition of the copper solution, and it ought only to be boiled gently for a minute or two, as several substances besides sugar separate suboxide of copper from alkaline solutions of oxide of copper if the boiling is prolonged. A counter experiment ought therefore always to be made by leaving at rest one half the mixture of urine, potash, and copper, *before it has been warmed,* for six to twenty-four hours without being heated, if sugar is present in the urine a separation of suboxide of copper will also take place in this mixture. Sugar is the only substance which can be present in the urine which reduces the oxide of copper without heat.

884. *Fermentation test.*—Fermentation is frequently em-

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* An excess of potash is productive of no harm.

† The solution of the copper salt ought to be so dilute as only to have a faintly blue tinge. Instead of sulphate of copper, Drs. Taylor and Brande recommend tartrate of copper, which is certainly to be preferred to the sulphate; they recommend recently precipitated tartrate of copper to be dissolved in a solution of soda or carbonate of soda. Tartrate of copper is more easily decomposed than the sulphate, less boiling is therefore required, which is a great advantage.

ployed as a test for the presence of sugar. "When used merely as a qualitative test to indicate whether sugar is or is not present in urine, the following is the simplest way of applying it. Fill a test-tube with the suspected urine, having previously mixed with it a few drops of fresh yeast, or still better, a little of the dried German yeast; close the open end with a small saucer or evaporating dish, and while gently pressing the latter upon the tube invert them. A little more of the urine is then poured into the saucer in order to prevent the escape of any of the liquid from the tube, and if any bubbles of air have accidentally been allowed to enter, the exact height of the upper surface of the liquid in the tube must be marked with ink or with a strip of gummed paper. The tube with its contents is then set aside in a warm place having a temperature of about 70° or 80° F. for twenty-four hours. If sugar is present it begins almost immediately to undergo the vinous fermentation, the carbonic acid as it is formed rises in minute bubbles, causing gradual and gentle effervescence, and collects in the upper tube, displacing an equal volume of liquid which escapes through the open end of the tube into the saucer. When the quantity of sugar present is at all considerable, the urine, after fermentation, will be found to possess a faint vinous smell. As bubbles of gas are sometimes given off by the yeast itself, it is a good precaution to put the same quantity of yeast into a second tube of equal size and fill it up with pure water. The amount of gas, if any, derived from the yeast will thus be rendered apparent, and may afterwards be deducted from the volume of gas in the tube containing the urine."—*Bowman.*

Inosite $C_{24}H_{24}O_{24}$.

885. "This sugar occurs in almost all parts of the animal system and is identical with phaseomanite, which occurs in unripe beans. It forms prismatic crystals of the form of gypsum; it is soluble in water; but insoluble in alcohol and ether; it has a sweet taste; it is not susceptible of the vinous

fermentation, but with chalk and cheese it yields lactic and butyric acids. It does not reduce oxide of copper. If it be evaporated with nitric acid nearly to dryness, and then mixed with a little ammonia and chloride of calcium, and again evaporated, a beautiful rose tint is produced, which is quite characteristic of it."

ALKALOIDS.

Urea, Kreatinine, Kreatin.

886. The only bodies we shall notice belonging to this class are the three given in the list; kreatin is neutral to test paper, but it has been combined with acids, and has the characters of a weak base. It will be seen that it is closely connected with kreatinine. The three substances possess no marked properties which are common to the three.

Urea, $(C_2H_4N_2O_2)$.

887. "This important compound is an essential constituent of the urine of animals; it is abundant in that of the mammalia and particularly so in the urine of the carnivora; but it has also been met with in the urine of birds and of amphibia. Urea is the principal outlet for the nitrogen of the system, after the materials which compose the animal tissues have experienced oxidation under the influence of the respired air, a healthy human adult excreting about an ounce of urea daily. Urea is not formed in the kidneys; these glands appearing to act somewhat in the manner of filters, by means of which the urea is separated from the mass of the blood, in which it exists already formed before reaching the kidneys."—*Miller*.

888. Urea can be formed *artificially* in a variety of ways; one of the simplest methods for its formation is by evaporating cyanate of ammonia, which is metameric with urea, at a gentle

heat; by a mere alteration of the elements of cyanate of ammonia urea is formed as shown in the following equation:

$$\underbrace{\mathrm{NH_4O, C_2NO}}_{\text{Cyanate of ammonia.}} = \underbrace{\mathrm{C_2H_4N_2O_2}}_{\text{Urea.}}.$$

889. Urea is formed whenever cyanic acid or cyanates come in contact with ammonia or ammoniacal salts. It is also formed by the spontaneous decomposition of an aqueous solution of cyanogen. Cyanate of ammonia is first formed, and this body becomes converted into urea as the liquid evaporates. It is also formed when ammonia is acted upon by phosgene gas (CO, Cl).

890. Béchamp has recently succeeded in preparing urea from albumen, by subjecting it to the oxidizing action of permanganate of potash.

891. "A solution of urea, *if pure*, may be kept at ordinary temperatures *without alteration*, and it may even be boiled without undergoing decomposition; but if heated in a sealed tube to about 284° F. it combines with four equivalents of water and is converted into carbonate of ammonia:"

$$\underbrace{\mathrm{C_2H_4N_2O_2}}_{\text{Urea.}} + \mathrm{4HO} = \underbrace{\mathrm{2(NH_4O, CO_2)}}_{\text{Carbonate of ammonia.}}.$$

The same change takes place slowly at ordinary temperatures in the presence of the mucus of the bladder, the ammoniacal odour acquired by urine after keeping it for a few days being due to this alteration. A similar decomposition into carbonic acid and ammonia occurs when urea is fused with hydrate of potash, or treated with concentrated sulphuric acid.

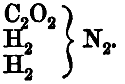
892. "Chlorine, when transmitted into an aqueous solution of urea, resolves the latter into carbonic acid and nitrogen, whilst hydrochloric acid is formed:"—

$$\mathrm{C_2H_4N_2O_2 + 2HO + 6Cl = 2CO_2 + 2N + 6HCl}.$$

893. Nitrous acid decomposes urea immediately into carbonic acid, nitrogen, and water :—

$$C_2H_4N_2O_2 + 2NO_3 = 2CO_2 + 4N + 4HO.$$

894. A variety of views have been adopted at different times as regards the constitution of urea; but it is now regarded as a diamine, two equivalents of hydrogen in diammonia being replaced by a diatomic radical, carbonyl. This view is supported both by its formation and products of decomposition.* Its formula, viewed as a diammonium compound, is



$$\left.\begin{matrix}C_2O_2\\H_2\\H_2\end{matrix}\right\}N_2.$$

895. Urea crystallizes in flattened four-sided prisms; they generally resemble nitre in appearance, and have a similar cooling, saline taste; they are inodorous. They are soluble in their own weight of cold water and in every proportion in hot water; they dissolve in 4·5 of cold and in two parts of boiling alcohol; but they are insoluble in ether and in an excess of strong nitric acid. Its solution is neutral to test-paper.

896. Urea is basic in its characters although neutral to test-paper; it combines with acids to form salts, some of which are crystalline. "Of these, the two which are of the most practical importance, are the oxalate ($C_2H_4N_2O_2$, HO, C_2O_3), and the nitrate ($C_2H_4N_2O_2$, HO, NO_5), which, on account of their sparing solubility in water, supply a ready means of separating urea from the other matters co-existing in the urine.

897. "*Oxalate of urea* ($C_2H_4N_2O_2$, HO, C_2O_3) may be prepared by concentrating urine on a water-bath to about one eighth of its bulk, and filtering through muslin, in order to separate the insoluble sediment of phosphates and urates, which are gradually deposited during the evaporation. The liquid thus clarified, is mixed with about an equal bulk of a

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* See the author's 'Second Step in Chemistry,' par. 1061.

strong solution of oxalic acid in hot water, or the solid acid in powder may be added as long as the liquid, heated to about 190° or 200° F., continues to dissolve it. The mixture, on cooling, deposits an abundant crop of crystals of oxalate of urea, mixed with a little of the excess of oxalic acid, and coloured brown by the adhering impurities. The crystals are then gently pressed between folds of filtering paper, washed with a small quantity of ice-cold water, and purified by recrystallization; the last traces of colouring matter being removed, if necessary, by boiling the solution with animal charcoal.

898. "The oxalate thus obtained is colourless, and in the form of tabular or prismatic crystals, which are readily soluble in hot water, but only sparingly so in cold, twenty-five parts of which dissolve not more than one part of the salt.

899. "*Nitrate of urea* ($C_2H_4N_2O_2$, HO, NO_5) may be obtained by adding strong colourless nitric acid, free from nitrous acid (893), to urine previously concentrated by evaporation to about one third its bulk; the nitrate gradually separates in irregular rhomboidal plates, more or less coloured and modified in form by the impurities present. The crystals are washed with a little ice-cold water, then pressed between folds of filtering paper, and redissolved in lukewarm water; lastly, they are purified by recrystallization, and if necessary, the last traces of colouring matter may be removed by boiling the solution with animal charcoal.

900. "Nitrate of urea is soluble in about eight times its weight of cold water, and in a much smaller quantity of hot. It is tolerably soluble also in alcohol, especially when warm, but almost insoluble in ether.

901. "The formation of this crystalline compound on the addition of nitric acid, is one of the most distinctive tests for the presence of urea which we possess. The experiment is made easily, and with great delicacy, under the microscope, by concentrating a drop or two of urine on a glass slide, and adding to it about an equal quantity of pure nitric acid; the nitrate will gradually crystallize in delicate rhomboidal plates, the number and abundance of which will furnish

some indication of the quantity of urea present in the secretion."*

KREATININE ($C_8H_7 N_3O_2$).

902. This substance is a powerful organic base; its aqueous solution restores the blue colour to reddened litmus paper, and when heated with solutions of ammoniacal salts it expels the ammonia like the fixed inorganic alkalies. It forms colourless prismatic crystals, and its salts are also crystalline. It dissolves in about twelve parts of cold water; it is much more soluble in hot water; it is very soluble in boiling alcohol but much less so in cold alcohol, it therefore crystallizes out as the boiling solution cools.

903. It has a strong tendency to form basic double salts; example: if a solution of nitrate of silver, moderately concentrated, be mixed with one of kreatinine, it becomes converted into a magma of white needles, which are very soluble in boiling water, and a similar compound is formed when a solution of corrosive sublimate is substituted for that of nitrate of silver. On the addition of a concentrated solution of chloride of zinc to a solution of this base, a double compound ($C_8H_7N_3 O_2$, ZnCl) is precipitated in a crystalline form; when very slowly formed the crystals are distinctly prismatic, but when quickly produced, and as seen under the microscope, fine needles are observed concentrically grouped together, forming either perfect rosettes, or tufts which cross each other, or of which each two are connected by thin short stalks, so as to resemble brushes passing one into the other. As chloride of zinc is the test usually employed to detect this base, it is important to observe that the double compound of zinc and kreatinine is not precipitated on the addition of the zinc chloride to the chloride of the organic base; but that the separation at once takes place, if before the addition of the chloride of zinc solution, a sufficiency of acetate of soda is mixed with the kreatinine salt.

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* Bowman's 'Medical Chemistry.'

904. This base has been found in the juice of muscle, in the blood as well as in the urine. Kreatin is converted into this body, kreatinine, by the action of strong acids.

KREATIN ($C_8H_9N_3O_4 + 2HO$).

905. In its pure state, this substance forms brilliant, colourless, prismatic crystals which become dull by loss of water at 212° F. It has a bitter, pungent taste. It dissolves in seventy-five parts of cold water. Boiling water takes up a much larger quantity of it, but as it cools, the kreatin separates in the crystalline form. Alcohol takes up only one part in 9410 parts; and in ether it is completely insoluble. In an impure state the solution readily putrefies.

906. It dissolves without change in dilute mineral acids; but when boiled with concentrated acids, it gives off water, and is converted into kreatinine.

$$C_8H_9N_3O_4 + 2HO - 4HO = C_8H_7N_3O_2.$$

907. Chloride of zinc produces no precipitate with perfectly pure kreatin; but if kreatinine is present, a triple compound consisting of chloride of zinc, kreatin and kreatinine, is precipitated in the form of radiating crystals.

908. This substance is found in the juice of muscles; and it is also found in the urine.

ACIDS.

LACTIC ACID, HIPPURIC ACID, GLYCOCHOLIC ACID, HYOCHOLIC ACID, TAUROCHOLIC ACID.

909. These acids are grouped together simply on account of their acid character.

LACTIC ACID ($2HO, C_{12}H_{10}O_{10}$.)

910. This acid is very much diffused in the animal frame; it

is found in the free state or combined in the muscle, the blood, the urine, the gastric juice, and in the yelk of the egg. It is also found in vegetable matters which have turned sour.

911. In its most concentrated state this acid is a colourless, inodorous, thick, syrupy fluid, which cannot be solidified by the most intense cold; its specific gravity = 1·215, it dissolves readily in water, alcohol, and ether, attracts water from the atmosphere, has a strongly acid taste and reaction, decomposes when heated, and displaces not only volatile acids, but even many of the stronger mineral acids from their salts. Heated with concentrated sulphuric acid, it yields almost pure carbonic oxide, and is converted into a substance resembling humin; it gives, however, no trace of formic acid.

912. With bases lactic acid generally forms neutral salts, all of which are soluble in water, and many in alcohol, but none in ether. Most of the lactates may be heated to 150° or 170° and some even to 210°, without undergoing decomposition. The alkaline lactates are not crystallizable, and by the greatest concentration can only be reduced to syrupy liquids; and the same is the case with the lactates of baryta, alumina, sesquioxide of iron, and binoxide of tin; but all other lactates crystallize with tolerable facility, and are capable of resisting the action of the atmosphere.

913. To determine the presence of lactic acid is one of the most difficult tasks in analytical animal chemistry, as is indeed evinced by the prolonged contest that existed regarding the presence or absence of this acid in the animal organism. In order to determine its presence with certainty, it must in the first place be separated from all other organic substances, but in this lies one of the great difficulties, for there is scarcely any other acid to which foreign bodies adhere so tenaciously (*Lehmann*).

914. The production of some of its salts and the inspection and examination of their form under the microscope supply the means for the detection of lactic acid; lactate of lime and lactate of zinc are the best suited for this purpose. Lactate of lime may be conveniently prepared from animal or vegetable

liquids by the following method devised by Scherer:—Dilute the liquid, if necessary, with water, mix with baryta-water, and filter. Distil the filtrate with some sulphuric acid (to remove volatile acids), digest the residue several days with strong alcohol, distil the acid solution with a little milk of lime, filter warm from the excess of lime and the sulphate of lime, conduct carbonic acid into the filtrate, heat once more to boiling, filter from the precipitated carbonate of lime, evaporate the filtrate, warm the residue with strong alcohol, filter, and let the neutral filtrate stand several days to give the lactate of lime time to crystallize. Should the quantity of lactic acid present be insufficient to allow the formation of crystals, evaporate the fluid to a syrupy consistence, mix with strong alcohol, let the mixture stand some time, decant or filter the alcoholic solution into a vessel that can be closed, and add gradually a small quantity of ether. The process will cause even minute traces of lactate of lime to separate from the fluid. Lactate of lime shows under the microscope the form of minute crystalline needles aggregated in tufts with short stalks, pairs of them always being joined at the stalked ends, so as to look like brushes united together.

915. Lactate of zinc deposited quickly from its solution shows under the microscope the form of spherical groups of needles. The slow evaporation of solution of lactate of zinc gives first crystals resembling clubs truncated at both ends; these crystals gradually increase in size; the two ends apparently diminish, whilst the middle parts increase in size (*Funke*).

HIPPURIC ACID ($HO,C_{18}H_8NO_5$).

916. This acid occurs in combination with potash or soda in the urine of man and herbivorous animals.

917. This acid is considered to be the amidogen compound of benzo-glycolic acid (glyco-benzoic acid), because, when treated with nitrous acid, it undergoes the decomposition peculiar to amidogen compounds, viz., the formation of a non-

nitrogenous acid, water, and the liberation of nitrogen. The acid formed on treating hippuric acid with nitrous acid, is benzo-glycolic acid (HO, $C_{18}H_7O_7$). Under the influence of boiling water benzo-glycolic acid splits up into benzoic and glycolic acids.

918. When hippuric acid is boiled for some hours with concentrated hydrochloric acid, it assimilates the elements of water and is resolved into benzoic acid and glycocine :—

$$\underbrace{HO,\ C_{18}H_8NO_5}_{\text{Hippuric acid.}} + 2HO = \underbrace{HO,\ C_{14}H_5O_3}_{\text{Benzoic acid.}} + \underbrace{HO,\ C_4H_4NO_3}_{\text{Glycocine.}}.$$

919. Hippuric acid has been artificially made by acting upon the oxide of zinc compound of glycocine with chloride of benzoyl :—

$$\underbrace{ZnO,\ C_4H_4NO_3}_{\substack{\text{Oxide of zinc and}\\ \text{glycocine.}}} + \underbrace{C_{14}H_5O_2 + Cl}_{\text{Chloride of benzoyl.}} = ZnCl + \underbrace{HO,\ C_{18}H_8NO_5}_{\text{Hippuric acid.}}.$$

920. This acid crystallizes in rhomboidal prisms, or in thin plates. It is sparingly soluble in cold water, one part requiring 400 parts for its solution; but it is very freely soluble in hot water. It is readily soluble in alcohol; but only sparingly soluble in ether, which distinguishes it from benzoic acid (598). Exposed to a high temperature it is decomposed into hydrocyanic acid, benzoic acid, benzoate of ammonia, and other products. Heated with a fragment of caustic potash it disengages ammonia. If placed in contact with ferments, it undergoes a kind of fermentation, the products of which are benzoic acid and ammonia.

921. Owing to this speedy conversion of it into benzoic acid and ammonia by ferments, it is not surprising that if the urine becomes in the slightest degree putrid, it is speedily decomposed into benzoic acid and ammonia. On the other hand, when benzoic acid is taken into the system, it is converted into hippuric acid, and is found in the urine in that state.

GLYCO-CHOLALIC ACID OR GLYCOCHOLIC ACID (*Cholic acid* of Strecker) HO, $C_{52}H_{42}NO_{11}$.

922. This acid, in combination with the fixed alkalies exists in the bile of man and other animals, but it is present in the greatest quantity in ox-bile. The acid is a white crystalline solid; it has a strong acid reaction, and a bitterish-sweet taste. It is more soluble in hot water than cold; alcohol dissolves it freely, but leaves it as a resinous mass on evaporation; it is very sparingly soluble in ether. The salts which it forms with the alkalies and alkaline earths may be crystallized; they are soluble in alcohol.

923. When this acid is boiled with an alkaline solution, as solution of potash or baryta, it is decomposed into glycocine (gelatine sugar), and a non-nitrogenous acid, called cholalic acid,[*] (the cholic acid of Demarçay):—

$$\underbrace{HO,\ C_{52}H_{42}NO_{11}}_{\text{Glyco-cholalic acid.}} + 2HO = \underbrace{HO,\ C_{48}H_{39}O_{9}}_{\text{Cholalic acid.}} + \underbrace{C_{4}H_{5}NO_{4}}_{\text{Glycocine.}}.$$

924. When it is boiled with concentrated sulphuric or hydrochloric acids, it is split up into glycocine and choloidinic acid ($C_{48}H_{38}O_{8}$ = cholalic acid − 2 eq. of water); if the ebullition with the acids be continued, the choloidinic acid is decomposed into a resinous substance, called, from its insolubility in water, *dyslysin* ($C_{48}H_{36}O_{6}$), and water.

HYOCHOLIC ACID (HO, $C_{54}H_{42}NO_{9}$).

925. Pig's bile differs from the bile of other animals, inasmuch as it contains hyocholic acid instead of glyco-cholalic acid; the former acid is decomposed like the latter by alkaline

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[*] This acid is soluble in sulphuric acid, and on the addition of a drop of this acid and a solution of sugar (one part of sugar to four of water) a purple-violet colour is produced which constitutes Pettenkofer's test for bile.

solutions and acids and into substances of analogous composition.

926. When it is boiled with an alkaline solution, it is decomposed for instance into glycocine and hyocholalic acid:—

$$\underbrace{HO,\ C_{54}H_{42}NO_9}_{\text{Hyocholic acid.}} + 2HO = \underbrace{HO,\ C_{50}H_{39}O_7}_{\text{Hyocholalic acid.}} + \underbrace{C_4H_5NO_4}_{\text{Glycocine.}}.$$

927. When it is boiled with acids it is decomposed into glycocine and a substance homologous with dyslysin, which is termed hyodyslysin ($C_{50}H_{38}O_6$).

Taurocholalic acid or Taurocholic acid (*Choleic Acid* of Strecker) HO, $C_{52}H_{44}NO_{13}S_2$.

928. The bile of man and most animals, with the exception of the ox and pig, consists mainly of taurocholalate of soda or potash. The alkaline salts of this acid are very soluble in water and alcohol. They give no precipitate with neutral salts of lead, but with the subsalts they deposit a plaster-like compound, which is soluble in boiling water. They yield with sulphuric acid and sugar a violet colour similar to that produced by the cholates.

929. When this acid is boiled with alkaline solutions it is decomposed into cholalic acid and taurine:—

$$\underbrace{HO,H_{52}C_{44}NO_{13}S_2}_{\text{Taurocholalic acid.}} + 2HO = \underbrace{HO,\ C_{48}H_{39}O_9}_{\text{Cholalic acid.}} + \underbrace{C_4H_7NO_6S_2}_{\text{Taurine.}}.$$

930. When it is boiled with acids it is decomposed into taurine* and choloidinic acid or dyslysin, according to the duration of the experiment.

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* The student is referred to the author's 'Second Step in Chemistry,' page 525, for an account of Kolbe's important experiments on the constitution of taurine.

CYSTINE, XANTHINE, AND CHOLESTRIN.

931. These three substances are met with in *calculi*.

932. Cystine ($C_6H_6NS_2O_4$).—This substance is met with nowhere but in the urine; it was originally discovered by Wollaston in a urinary calculus; calculi of this nature, although very rare, have since been found by many other chemists. "It occurs in colourless, transparent, hexagonal plates or prisms; it is devoid of taste and smell, and is insoluble in water and alcohol. It dissolves in oxalic and the mineral acids, forming with them saline combinations, most of which are crystallizable, but it does not unite with acetic, tartaric, or citric acid; it is decomposed by nitric acid, leaving on the evaporation of the fluid, a reddish-brown mass; it dissolves freely in the caustic fixed alkalies and their carbonates. It dissolves in caustic ammonia, but does not unite with it, so that on evaporation it crystallizes unchanged. It is insoluble in carbonate of ammonia; hence it is best precipitated from its acid solutions by carbonate of ammonia, and from its alkaline solutions by acetic acid.

933. "Cystine does not fuse on the application of heat, but it burns with a *bluish-green flame*, developing at the same time a very peculiar acid odour; on dry distillation it develops a stinking empyreuma and ammonia, and leaves a voluminous porous coal. On boiling it with alkalies, ammonia is first developed, and subsequently an easily inflammable gas, which burns with a blue flame.

934. "Cystine is characterised by the readiness with which it crystallizes in well-formed hexagonal plates, which may be distinguished with great ease under the microscope, and by its solubility both in alkalies and mineral acids. Further, it may be known by the peculiar odour which it develops on dry distillation and on burning, which is unlike that evolved by any other similar substance. Liebig has given the following test for cystine. The potash-extract of the substance in which we

are searching for cystine must be decomposed with a solution of oxide of lead in caustic potash; if, on the application of heat, there be a precipitation of sulphide of lead, cystine is probably present; we must, however, previously satisfy ourselves that no other organic substance containing sulphur, as for instance, albumen, mucus, &c., be simultaneously present.

935. "If cystine be mixed with a small quantity of the urates, the two substances may be separated by the aid of boiling water, in which the former is insoluble. Uric acid occasionally appears under the microscope in the form of hexagonal tablets, but we should never trust in these cases to microscope examination alone."—*Lehmann.*

936. XANTHINE OR XANTHIC OXIDE ($C_{10}H_4N_4O_4$).—This substance has also been named *uric oxide* and *urous acid* owing to its being regarded as uric acid in a lower stage of oxidation. It is the principal constituent of a very rare variety of urinary calculus. It is one of the products in the decomposition of guanine, a substance found in guano and in the excrement of the garden spider. "It is likewise present in nearly every part of the animal organism, and, although in very minute quantities, in urine. It is a white amorphous powder, and it acquires a waxy lustre on friction with a hard body. It is very slightly soluble in water; it is insoluble in alcohol and ether. It dissolves easily in ammonia. It also dissolves freely in the fixed alkalies; carbonic acid separates it from its alkaline solution. It is all but insoluble in hydrochloric and oxalic acids; it is soluble in sulphuric and nitric acids. It dissolves in nitric acid without disengagement of gas, and gives on evaporation a yellow residue, which, on addition of ammonia or potash, turns yellowish red. From the circumstances under which it occurs it can only be confounded with cystine or uric acid; it differs from these by its amorphous condition. It is distinguished from cystine by its insolubility in hydrochloric and oxalic acids. It is distinguished from uric acid by its solubility in ammonia, and by the residue obtained on evaporating its nitric acid solution not turning red on the addition of ammonia.

937. **Cholestrin.**—"This substance is found in small quantity in various parts of the animal system, as in the bile, in the brain and nerves, and in the blood. It forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling the cholestrin crystallizes in brilliant colourless plates. It has the physical characters of a fat, is insoluble in water, tasteless and inodorous; it is freely soluble in boiling spirit and also in ether. It is not saponified by potash; thus differing from other fatty and oily substances which it resembles in many respects. It melts at 278·6° F., and contains probably $C_{26}H_{22}O$, or $C_{52}H_{44}O_2$."

COLOURING MATTERS.

938. We group together the colouring matter of the urine, the bile, and the blood.

939. *Colouring matter of the urine.*—"The colouring matter of the urine is constantly undergoing change; by means of neutral and basic acetate of lead it may be separated into two substances which contain different amounts of carbon. The substance which contains most carbon may be obtained as a dark-blue powder; when dry it has a copper colour like indigo and dissolves in alcohol, giving a purple-blue solution. It is said to occur most evidently in Bright's disease. Virchow states that he met with this blue pigment in crystals in unhealthy urine. Three colouring matters have been distinguished in urine which have received the names of uroxanthin, uroglaucin, and urorhodin; they have not been perfectly examined on account of the difficulty of preparing them. One of them has many of the properties of indigo."

940. *Colouring matter of the bile.*—"The principal colouring matter of the bile has been called *cholepyrrhin.* When dry it is reddish brown and uncrystallizable, insoluble in water, more soluble in alcohol, which becomes yellow, and most soluble in caustic alkali. On the addition of nitric acid to the yellow alkaline solution a change ensues. It passes through *green,*

blue, violet, and *red;* after some time it again turns yellow, probably in consequence of a gradual process of oxidation."

941. Another colouring matter has been called *biliverdin.* It is dark green, amorphous, without taste or smell, insoluble in water, slightly soluble in alcohol, but soluble in ether. Berzelius considers it to be identical with the chlorophyll, or green colouring matter of leaves.

942. *Colouring matter of the blood.*—The red colouring matter of the blood-corpuscles is called hæmatin or hæmatosin; it leaves when burnt a residue of peroxide of iron and phosphate of lime. It is unaffected by dilute ammonia, but is entirely destroyed by ebullition, with the formation of a dirty-coloured coagulum, which dissolves in caustic potash with an indistinct greenish colour.

943. *Tests for blood.*—"Blood-stains on articles of clothing may be identified—1. By their peculiar crimson-red colour. 2. By the shining and raised surface of the stain or spot (dried albumen and fibrin). 3. By their ready solubility in water, to which they give a red colour. The water under these circumstances contains albumen as well as hæmatosin. Weak ammonia does not change the red colour to a *blue, green,* or *crimson* tint. When boiled, the albumen and hæmatosin are both coagulated, and the red colour is entirely destroyed; a muddy brown coagulum subsides which is quite insoluble in water and alcohol. For the examination of such stains in a dry state, an inch power of the microscope will be found convenient.

944. "By employing a small quantity of water on a glass slide in order to dissolve the stain, the clot may be broken up and the red corpuscles separated. These may be examined by a quarter-inch power under the microscope. When detected, the evidence of the presence of blood is placed beyond doubt. No other red colouring matter, vegetable or animal, owes its colour to corpuscles or cells. A small quantity of glycerine added to the water which is used as a solvent prevents it from drying too rapidly."—*Brande and Taylor.*

945. *Test for bile.*—Bile is essentially composed of soda

salts of the two acids, glycocholic and taurocholic, cholestrin, mucus, and colouring matter. It is a ropy, viscid, and saponaceous liquid of a greenish-yellow colour in man, greenish brown in the ox, and emerald or grass-green in birds, reptiles, and fish. It has a bitter taste and an offensive odour. Its reaction is generally alkaline, it is sometimes neutral but never acid, excepting in peculiar states of disease. It mixes in all proportions with water, it is not coagulated by heat. Alcohol renders it turbid by precipitating the mucus.

946. We have noticed that the two acids in the bile when treated with sulphuric acid and sugar acquire a purple colour. Upon this reaction a test, called Pettenkofer's test, for bile has been founded. The best mode of applying the test for the detection of small quantities of bile in blood or other animal fluids is as follows:—The alcoholic extract of the liquid to be tested for biliary matter is dissolved in a little water and mixed with a single drop of a solution of sugar (one part of sugar to four parts of water), and pure strong sulphuric acid is then added in small quantities till the turbidity at first produced disappears, cooling after each addition; it then for a few moments exhibits a yellowish colour, which, however, soon changes to a pale cherry-red, then to deep carmine, then to purple, and finally to an intense violet tint. For the success of the experiment, care must be taken not to add too much sugar, otherwise a black mass will be formed which will completely mask the reaction. The temperature of the mixture must be allowed to rise to about 106° F., but not higher. The reaction takes place with any kind of sugar and likewise with acetic acid.

A METHOD FOR ANALYSING QUALITATIVELY THE SECRETIONS OF ANIMALS.*

947. The physical characters, such as colour, taste, odour, consistence, &c., should first be carefully observed. The spe-

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* The method for analysing the animal secretions, and for the analysis of urine, has been taken mainly from Gerhardt and Chancel's 'Qualitative Analysis.'

cific gravity may also be ascertained, when it can conveniently be done, as a knowledge of the density of the fluid will serve to furnish some indication of the amount of solid matter held in solution.

948. The liquid should be examined by test-papers whether it is neutral, alkaline, or acid.

949. When the liquid holds in suspension any solid or semi-solid matter the dissolved should be separated from the undissolved portion either by decantation or by filtering it through paper or fine muslin. The microscopic examination of the residue always furnishes some useful indications. The spontaneous coagulation in a secretion, at first limpid, is due almost always to fibrine.

950. The clear liquid is then submitted to the following examinations:—

951. *First examination.*—We heat a portion of the liquid in a test tube; when the liquid is neutral or alkaline, one or two drops of acetic acid is first added. If the liquid remains clear on warming it, we can be certain of the absence of albumen; in that case we pass on to the second examination.

952. If, on the contrary, the liquid becomes troubled or coagulated, it becomes necessary, after having agitated it, to divide it into two portions and add to one a few drops of dilute hydrochloric acid. If the precipitate disappears it has not been due to albumen but was probably due to phosphate of lime, or magnesia, or both. The other portion of the liquid must be examined by the microscope.

953. When the dilute hydrochloric acid does not redissolve the precipitate, we then add a larger quantity and finally boil the mixture; if the precipitate becomes slowly dissolved and the liquid assumes a violet colour (782), this reaction indicates the presence of *albumen*. We control this result by examining the action of nitric acid upon the primitive secretion (781 and 807).

954. When the secretion upon which we operate, or the coagulum which it gives possesses a reddish tint, there can be present hæmatine and also globulin. In this case, we dry the

coagulum; it then assumes a brown or black tint. It is afterwards boiled with alcohol to which a little sulphuric acid has been added; if it contains hæmatine, the liquid is coloured red, and the alcoholic extract after having been evaporated to dryness furnishes a residue which gives after calcination, the reactions of iron (941).

955. *Second examination.*—A liquid which does not contain albumen, or from which it has been separated by coagulating the albumen and then filtering, can yet contain caseine and globulin. To ascertain whether these substances are present, we treat a small quantity of the liquid free from albumen with ferrocyanide of potassium. If the liquid remains clear it does not contain any of the members of the albuminous group. If it is rendered turbid, we treat a portion with a solution of chloride of calcium and boil the mixture, which renders it turbid if *caseine* is present (835): when this effect is manifested we digest the liquid with rennet at a temperature of 104° F., in order to render the coagulation of the caseine complete.

956. If the secretion contains also globuline, it will be rendered turbid by the addition of a few drops of acetic acid, and gives afterwards a flaky precipitate when neutralized with ammonia (837).

957. *Third examination.*—If the preceding examinations have shown that the liquid contains albuminous matter, we commence this examination by coagulating, and then filtering, and afterwards boiling the liquid and continuing the evaporation until its volume has been reduced to one half.

958. If, on the cooling of the liquid, a precipitate is not formed, we conclude that *urates* are probably absent; these salts, being moreover very little soluble, are ordinarily found in the sediment which is spontaneously deposited in the liquid; we pass then to the fourth examination.

959. If, on the cooling of the liquid, a deposit of any kind is formed, we first examine by the microscope; if it is amorphous we treat a portion with acetic acid, and we again examine it with the microscope; if rhombic tables are seen they indicate the presence of uric acid. To confirm this result, the rest of

the deposit is dissolved in nitric acid and examined for uric acid as directed in par. 635.

960. If the deposit is crystalline and does not change its form by acetic acid, it is formed of *sulphate of lime* or phosphate of magnesia. We prove the presence of these salts by their reactions.

961. *Fourth Examination.*—The liquid, freed from the deposit by filtration, is evaporated to dryness on the water bath, and the residue is treated with alcohol of a density of 0·83. The alcoholic solution and the substance insoluble in alcohol are separately examined.

962. *The alcoholic solution* is submitted to the following examinations:

1. To a small portion of this solution is added drop by drop, fuming nitric acid (containing nitrous vapours); if there is formed after the addition, at the bottom of the liquid a zone at first green, next blue, violet, red, and lastly of a dirty yellow, it proves the presence of the *colouring matter of the bile* (940).

2. Another portion is mixed with sugar and sulphuric acid; a beautiful purple-red colour proves the presence of *the acids in the bile* (946).

3. In a third portion, we look for *glucose.* This substance generally communicates to the liquid a sweet taste. This portion of the alcoholic solution is evaporated to dryness on the water bath, the residue is redissolved in water and examined for glucose by the copper test (882 and 883). The result ought to be controlled by the fermentation test (884).

4. The greater part of the alcoholic solution is evaporated to a very small volume, it is then mixed with *pure* nitric acid, which must be free *especially* from nitrous acid, and we place the vessel in a cooling mixture. If a crystalline deposit is formed, it is examined by the microscope to ascertain whether it has the appearance of nitrate of urea (899 to 902) or of hippuric acid. The indications obtained by the microscope are confirmed by the chemical reactions.

5. A portion of the *concentrated* alcoholic solution is mixed with a syrupy solution of chloride of zinc, if a precipitate is not

formed even after a length of time, the liquid does not contain kreatine. If a precipitate is produced, we submit it to some special examinations, to ascertain the presence of kreatine or kreatinine.

6. Lastly, if the alcoholic solution possessed a strong acid reaction, it has still to be examined for lactic acid. To effect this the extract is concentrated and heated along with oxide or carbonate of zinc; a drop of the boiling filtered liquid is placed between two plates of glass, and we examine it by the microscope to see if the characteristic crystals of lactate of zinc are formed.

963. *Insoluble residue.*—In addition to *mucus* and undefined *extractive matters*, this residue can contain uric acid, a little casein, &c.

964. *Fifth Examination.*—After having finished the previous examinations, a portion of the *original* solution is evaporated to dryness on the water bath and the residue treated with ether. This dissolves the fatty matters, the presence of which we ascertain by evaporating the etherial solution.

965. The portion insoluble in ether must be incinerated in a platinum crucible, and the inorganic salts determined by the ordinary methods.

QUALITATIVE ANALYSIS OF URINE.

966. The preceding method can, with some slight modifications be applied to the analysis of most of the animal secretions.

967. Of the secretions, the urine presents a particular interest for the medical practitioner, owing to the changes which it undergoes in its composition by the effects of certain diseases, and which can be made use of as a means of diagnosis.

968. The bodies which normal urine holds in solution in water are—

Organic Substances.

Urea.
Uric acid.
Hippuric acid.
Kreatine.
Kreatinine.
Colouring and extractive matters.
Mucus of the bladder (in suspension).

Mineral Substances.

Salts of
  Potash.
  Soda.
  Lime.
  Magnesia.
  Iron.
Silicates.
Phosphates.
Sulphates.
Chlorides.

969. We find in addition, in normal urine, very small quantities of ammonia and of carbonic acid gas.

970. Recently emitted, it always possesses an acid reaction,* due very probably to the presence of hippuric or uric acid. It behaves with reagents in the following manner:

1. It is not coagulated by *boiling*.
2. The *caustic alkalies* on being added to it, produce a turbidness, or a precipitate of the phosphates of the alkaline earths.
3. *Chloride of barium* gives a precipitate of sulphate and phosphate of baryta.
4. *Nitrate of Silver* gives a precipitate of chloride and phosphate of silver.
5. *Acetate of Lead* gives a precipitate of phosphate, sulphate and chloride of lead.
6. *Oxalate of Ammonia* gives a precipitate of oxalate of lime.
7. *Alcohol* determines a turbidness which disappears by the addition of a sufficient quantity of water.

971. The following substances are only contained in the urine in certain diseases:

1. Carbonate of ammonia. Lactic acid. Albumen (in many

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* The experiments of Dr. Bence Jones show that when passed shortly after eating, the urine is often neutral, or even alkaline, becoming again gradually more and more acid up to the time when the next meal is taken.

diseases). Fibrine (found only in the sediments). Fatty substance (very rarely). Colouring matter of the bile (in liver complaints). Acids of the bile rarely. Glucose (diabetes). Sulphuretted hydrogen (very rarely). Oxalate of lime and cystine.

972. Before proceeding to the examination of the substances contained in the urine, it is necessary to observe the colour, the transparency, the odour, the action upon test-paper. When the urine possesses an alkaline reaction, it is necessary to note if it is fresh, or if it is already commencing to undergo putrefaction.

973. It is equally useful to determine its density; the density of healthy human urine varies from 1,005 to 1,030.

974. After having obtained this preliminary information, we allow a quantity of the urine to stand for some time in order to allow time for the formation of a sediment. We then filter and examine separately the filtrate and the sediment.

975. *The filtrate.*—A quantity of the urine is boiled in order to coagulate the albumen * when it is present, after that we examine the filtered liquid as described in par. 958. We at first look for the normal constituents of the urine, such as uric acid, the urates, hippuric acid, and urea; lastly those which are accidental, as carbonate of ammonia, lactic acid, the colouring matter of the bile and glucose.

976. Carbonate of ammonia can only be present in urine which has an alkaline reaction. The urine, which contains this ammoniacal salt, effervesces on the addition of an acid; when the urine is boiled with potash, ammonia is disengaged, and is recognised by its reactions, (136).

977. Urine containing biliary matter is in general strongly coloured; its tint varies from saffron yellow, to yellowish brown; if the urine has a sediment, this is also coloured.

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* The precipitate produced by boiling is not a sure proof of albumen; since a white precipitate is also produced by boiling, when the urine (free from albumen) contains an excess of earthy phosphates; see pars. 952 and 953, for distinguishing the two precipitates.

When we agitate a sample of this urine, there is formed on the surface a yellow scum.*

978. Urine containing sugar is usually characterised by its high specific gravity, which is frequently from 1,030 to 1,045, and occasionally as high as 1,050 and 1,055. If, however, the sugar is present only in small quantity, the specific gravity may not be higher than usual; so that a moderately low specific gravity is of itself no proof of the absence of sugar. It is generally paler in colour than normal urine; and it is generally slightly turbid.

979. Urine containing fatty or chylous matter, is usually more or less turbid, and frequently has an almost milky appearance.

980. Urine containing sulphuretted hydrogen, has the odour of rotten eggs; test for it as directed in par. (460).

981. *Sediments.*—The sediments ought to be examined microscopically as well as chemically.

982. The bodies contained in urinary sediments are—

Uric acid; the urates (of lime, magnesia, potash, soda, and ammonia). Oxalate of lime. Phosphate of lime and ammonio-phosphate of magnesia. Cystine. Different organic materials, such as mucus, blood, pus, spermatozoa, &c.

983. Free uric acid is only found in the sediments furnished by dark coloured urine, and it possesses a distinct acid reaction. These sediments are also coloured; they can have a pale tint, but it is generally yellow, orange yellow, or brown; they have a granular appearance, and frequently even visibly crystalline to the naked eye. The uric acid can be very well detected with the microscope, or by its reaction with nitric acid and ammonia (635). It is distinguished from the urates by its insolubility in water, and by the fixed residue which these leave on incineration; it is distinguished from urate of

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* The taste of urine containing biliary matter is remarkably bitter, a peculiarity which furnishes a ready indication of its presence when other tests are not at hand; though it must not be implicitly relied on, since small traces may exist in the secretion without communicating to it any very decided taste (Bowman).

ammonia by the latter disengaging ammonia in contact with potash.

984. The urates also form a part of the sediments deposited from acid urine. The colour of these sediments, as well as the urine, varies much. The urates contained in the sediments present frequently, to the naked eye, the appearance of mucus, of pus, and of blood, and can be distinguished only from these matters by microscopic observation and chemical analysis. Urate of soda is the one most frequently met with.

985. Oxalate of lime can make part of the sediment furnished by urine, the reaction of which is acid, neutral or alkaline, and it is not rare to find it associated with the urates. The urine containing oxalate of lime possesses a coloration, sometimes clearer, sometimes darker than that of normal urine; its colour is frequently that of amber yellow. Oxalate of lime, obtained by double decomposition, is an amorphous powder, whilst that found in the urinary sediments is distinguished by its crystalline form. The identity of oxalate of lime is easily determined by the aid of its chemical reactions; when it is heated upon platinum foil, it is transformed into carbonate of lime without carbonization.

986. The phosphates of the alkaline earths are easily identified by their chemical reactions. (*See* par. 262.)

ANALYSIS OF CALCULI AND CONCRETIONS.

987. The number of substances which compose the calculi and concretions of animals is not considerable; the most frequent are:

Uric acid and the urates.
Xanthine.
Cystine.
Hippurate of ammonia.
Phosphate of lime.
Ammonio-phosphate of magnesia.
Oxalate of lime.
Carbonate of lime.
Carbonate of magnesia.
Cholesterin (with other fatty matters).
Colouring matter of the bile.
Fibrine.

988. The preceding substances are accompanied by the following bodies:

The acids of the bile.	Extractive matters.
Albumen.	Soluble salts.
Mucus.	

989. The manner in which calculi comport themselves when calcined upon a platinum foil by the aid of heat, permits of their division into many groups:

CALCULI WHICH DO NOT LEAVE A FIXED RESIDUE.

990. *Calculi entirely combustible.*—They can be formed of uric acid, of urate of ammonia, hippurate of ammonia, of xanthine, of cystine, of cholesterin, of the colouring matter of the bile, of fibrine, or of albumen.

CALCULI WHICH LEAVE A FIXED RESIDUE.

A. *Calculi partially combustible.*—They can contain urate of soda, urate of lime, and all the organic matters quoted in combination with mineral substances.

B. *Calculi entirely fixed.*—They cannot contain any organic matter.

991. CALCULI WHICH DO NOT LEAVE A FIXED RESIDUE.—We treat a portion of this material with concentrated nitric acid, we evaporate to dryness, and we moisten the residue with a drop of ammonia.

992. It is coloured purple-red:

We pour upon the calculus a solution of potash, no disengagement of ammonia.	URIC ACID.
In contact with the potash solution ammonia is disengaged.	URATE OF AMMONIA.

993. It is not coloured purple-red:

The nitric solution becomes *yellow* during the evaporation; the residue is insoluble in carbonate of potash.	XANTHINE.

The nitric solution is coloured dark brown by the evaporation; the residue dissolves in caustic ammonia, and deposits from this solution under the form of microscopic hexagonal tables.	**Cystine.**

994. The calculus is heated upon platinum foil; it takes fire and burns with a very clear white flame, it can consist of cholesterin or of fibrine.

The calculus possesses evidently a crystalline texture, it dissolves in boiling alcohol, and is deposited as the solution cools under the form of shining spangles; it is insoluble in caustic potash.	**Cholesterin.**
The calculus during the combustion develops the odour of burnt horn and becomes swollen; it dissolves in caustic potash from which acetic acid precipitates it; the precipitate dissolves in an excess of acetic acid, gives a solution which yields a precipitate with ferrocyanide of potassium.	**Fibrine.**

995. The calculus possesses a brown colour; it is friable, ochreous, and disengages the odour of calcined animal matter in burning.

It is little soluble in alcohol and water, it dissolves in potash which it colours dark brown; nitric acid produces, in this solution, change of coloration characteristic of the colouring matter of the bile.	**Colouring Matter of the Bile.**
It is soluble in alcohol; the solution possesses a bitter taste; with sulphuric acid and sugar it takes a beautiful reddish-violet colour.	**Acids of the Bile.**

996. Calculi which leave a fixed residue.—Two cases can present themselves:

A. The matter does not give, with nitric acid and ammonia, the reaction of uric acid. (*See* par. 635.)

a. The residue from the calcination melts easily by heat.

The calculus does not effervesce with acids either before or after the calcination; it dissolves in hydrochloric acid, ammonia precipitates it from this solution; oxalate of ammonia also precipitates it; heated with the blow-pipe flame, moistened with a solution of nitrate of cobalt and again heated, it furnishes a blackish-brown enamel.	**Phosphate of Lime.**

During the calcination the calculus disengages an ammoniacal odour; it dissolves without effervescence in acetic acid; ammonia forms in this solution a cystalline precipitate. Heated with the blow-pipe flame along with a solution of nitrate of cobalt, it furnishes a dark-red glass.	AMMONIO-PHOSPHATE OF MAGNESIA.

b. The residue from the calcination does not melt on being heated.

The residue is white and does not turn red litmus blue; it gives the reactions of phosphate of lime (par. 253).	PHOSPHATE OF LIME.
The original matter is not attacked by acetic acid; the mineral acids dissolve it without effervescence, and ammonia precipitates it from this solution; after calcination the residue possesses an alkaline reaction, and the acids then dissolve it with effervescence (see par. 254).	OXALATE OF LIME.
When heated by the blow-pipe flame the calculus becomes luminous; before calcination the acids dissolve it with effervescence; after the acid solution has been neutralized with ammonia it gives a white precipitate with oxalate of ammonia.	CARBONATE OF LIME.

B. The matter gives with nitric acid and ammonia, the reaction peculiar to uric acid (see par. 635).

a. It melts on being heated;

It communicates an intense yellow coloration to the flame.	URATE OF SODA.
It does not colour the flame yellow, and dissolved in hydrochloric acid, and then treated with bichloride of platinum in the manner directed in par. 141, it gives a yellow precipitate.	URATE OF POTASH.

b. It does not melt on being heated:

The residue after calcination comports itself as carbonate of lime.	URATE OF LIME.
The residue after calcination dissolves with a slight effervescence in dilute sulphuric acid; the solution neutralized by ammonia gives with phosphate of soda, a white precipitate.	URATE OF MAGNESIA.

997. When the nature of the calculus has been determined, it is always necessary to control the results by special reactions.

VEGETABLE CHEMISTRY.

998. We have given the properties and reactions of the chief members in the three following groups:—Albuminoid group; the saccharine or amylaceous group, and the group of the vegetable bases.

THE ALBUMINOID GROUP.

ALBUMEN, FIBRIN, CASEIN.

999. *Vegetable albumen.*—This substance exists in the juice of most vegetables, and in the solid form in certain parts of the plant, especially in the seed. It exhibits the reactions, and appears to have the same composition as animal albumen (797). "The mode of its occurrence differs, however, remarkably from that of animal albumen in this respect, that it is always found in plants in neutral or acid liquids, whereas animal albumen exists only in alkaline liquids."

1000. *Vegetable fibrine, gluten.*—This substance is also found in the juices of all nutritious vegetables. When the newly expressed juice is allowed to stand for a few minutes, the fibrine it contains separates in a coagulated state, more or less impure. The juice of grasses is especially rich in this constituent, but it is most abundant in the seeds of wheat and other corn plants. It may be obtained from wheat flour by a mechanical operation, and in a state of tolerable purity; it is then called gluten. It is a soft, glutinous and elastic substance, which can be drawn out into long strings; it has scarcely any colour, taste, or smell.

1001. It exhibits the same reactions, and has the same composition as animal fibrine (822).

1002. *Vegetable casein, legumine.*—This substance is found chiefly in the seeds of peas, beans, and similar leguminous seeds; hence it is frequently called *legumine.* Its composition has not been well determined, but Liebeg considers it to be identical with the caseine of milk, which it resembles in its reactions (829).

THE SACCHARINE OR AMYLACEOUS GROUP.

1003. The substances forming this group are numerous; they contain, with a few exceptions, oxygen and hydrogen in *the proportion* to form water. The sugars and gums are the only members of the group which are soluble in cold water; starch and other similar bodies are insoluble in cold, but soluble in hot water; whilst cellulose is quite insoluble in water, whether hot or cold.

1004. We may here observe that there are three leading varieties of sugar—CANE-SUGAR (*sucrose*), GRAPE-SUGAR (*glucose*), MILK-SUGAR (*lactose*), and some chemists add a fourth, Fruit-sugar or fructose; other chemists consider it to be merely grape-sugar.

1005. We have restricted our notice of this group to the following members:—CELLULOSE, STARCH, GUM, DEXTRINE, CANE-, and GRAPE-SUGARS.

CELLULOSE, (*Lignin, woody fibre,* $C_{12}H_{10}O_{10}$).

1006. Cellulose forms the framework of all plants; its composition and reactions are always the same, but the properties which depend upon its state of aggregation, present the greatest differences, as its texture varies with the plant from which it is extracted. Cotton, linen, hemp, and unsized white paper, consist of cellulose very nearly pure. "The easiest method of obtaining pure cellulose, is to wash white cotton, unsized paper, old linen, or elder-pith with a hot solution of caustic potash or soda, then with cold dilute hydrochloric acid, then with ammonia, washing thoroughly with water after the application of each of these reagents, and lastly, with alcohol and ether; it is often necessary to repeat this series of operations two or three times. To obtain pure cellulose from wood it is necessary, after boiling the wood with potash till the liquid is almost dry, to treat it with chlorine water, or with a weak solution of chloride of lime, repeating these successive operations several times, in order to free the cellular tissue from the encrusting matter which is so intimately united with it.

1007. "Cellulose thus purified is white, translucent, of specific gravity about 1·5, insoluble in water, alcohol, ether, and oils, both fixed and volatile. When quite pure it is unalterable in the air, but as it exists in wood, in contact with azotized and other easily alterable matters, it gradually decomposes in moist air, undergoing a slow combustion, and being converted into a yellow or brown friable substance called *touchwood.*"

1008. *Dilute* acids do not act on cellulose.

1009. *Cold concentrated sulphuric acid* disintegrates it and converts it into dextrine, a substance isomeric with cellulose, without blackening; if water be then added and the liquid be subsequently boiled, the dextrine is converted into glucose.

1010. *Concentrated nitric acid* transforms cellulose into gun-cotton.

1011. *Alkaline liquids* when dilute do not act upon cellulose but when concentrated they gradually destroy its texture.

1012. "Cellulose in its natural state, is not coloured blue by iodine; but after it has been digested for a short time with sulphuric acid, it becomes of a fine blue when free iodine is added. This reaction is sometimes serviceable in the microscopic examination of vegetable tissues; cellulose being thus easily distinguished from tissues, into the composition of which nitrogen enters. By the prolonged action of sulphuric acid, the property of being coloured blue by iodine disappears, the dextrine and sugar which are formed, not being susceptible of the blue coloration."

1013. Cellulose dissolves completely in an ammoniacal solution of oxide of copper,* forming a syrupy liquid, which may be filtered after dilution with an equal bulk of water. It is precipitated from this solution in flakes on the addition of hydrochloric acid.

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* Prepared by dissolving oxide of copper in ammonia.

STARCH, (*Amylum, Fecula*, $C_{12}H_{10}O_{10}$).

1014. This substance is deposited in grains in the cellular tissue of certain parts of plants. The form and dimension of the starch grains are tolerably uniform in size in the same plant, but are very variable in different species of plants.

1015. It is insoluble in *alcohol*, *ether*, and *cold water*, but when a mixture of starch and water is heated to near the boiling point, the granules burst and disappear, forming a gelatinous mass. If this paste be largely diluted with water, the swollen granules of the starch subside, whilst a certain quantity of amylaceous matter remains in solution.

1016. When dry starch is heated to about 400° F., it is converted into a substance isomeric with starch, called dextrine or British gum. This substance is soluble in cold water, forming a ropy solution much resembling gum in properties; but it differs from gum in forming a deep blue liquor in a solution of sulphate of copper, which deposits suboxide of copper when cold. It is rendered red and not blue with iodine. It has been called dextrine from its turning the plane of polarization to the *right*, when acting on polarized light.

1017. *Dilute alkalies and acids* in the cold cause starch to swell up and become partially disintegrated, but if the solution is heated it is converted into dextrine.

1018. An aqueous solution of iodine forms with starch a characteristic blue colour; this colour disappears if the iodine be added in excess, or if the solution be heated, but in the latter case, the blue colour returns as the liquid cools. The colour disappears also by alcohol, potash, sulphuretted hydrogen, sulphurous acid, and in general by all liquids which dissolve iodine.

GUM ($C_{12}H_{11}O_{11}$).

1019. This substance is found in the juices of almost all plants, but is met with in its purest form in transparent tears, which exude from various species of acacia. Gum-arabic may be taken as its type.

1020. The gums proper are soluble in cold water or hot; but *mucilage* or *bassorin*, a modification of gum, is insoluble in water, but when moistened with it, swells up into a gelatinous mass.

1021. *Alcohol* and *ether* precipitate gum from its solution in water, in the form of white flocculi, or if dilute, in the form of a milky turbidity.

1022. Caustic potash coagulates a solution of gum; but an excess of the reagent renders the liquid limpid.

1023. Concentrated nitric acid converts gum into mucic and oxalic acids.

1024. If it is boiled with dilute sulphuric acid it is transformed first into dextrin and then into glucose.

1025. If a few drops of sulphate of copper be added to a solution of gum mixed with potash, a blue precipitate is produced, which is insoluble in the liquid, but which is soluble in pure water, this solution can be boiled without depositing oxide of copper. This character distinguishes natural gum from dextrine (British gum).

CANE-SUGAR or *Sucrose* ($C_{12}H_9O_9 + 2HO$).

1026. This variety of sugar is widely spread in the vegetable kingdom; it has been called cane-sugar because it is obtained chiefly from the sugar-cane. It has a specific gravity of 1·6. It is soluble in about one third of its weight of cold, and is much more soluble in boiling water; its solution has, as is well known, a sweet taste. Absolute alcohol dissolves about 1-80th of this sugar at its boiling point, nearly the whole of which separates in small crystals on cooling. It is more soluble in ordinary alcohol. It slowly separates from a strong watery solution in large, transparent, colourless crystals, having the figure of a modified oblique rhombic prism; if a solution of it is kept at a temperature near the boiling point it gradually loses the property of crystallizing. It melts, about 320° F., into a viscous colourless mass, which, on cooling, forms the solid known as barley sugar; if long kept this amorphous form of cane-sugar gradually loses its transparency, and becomes crystallized. If, after the sugar has melted, the application of heat be continued, until the temperature reaches 400° or 429° F. the sugar loses two equivalents of water, and a *brown, deliquescent, slightly bitter* and *unfermentizable substance* called *caramel* remains, which is used as a colouring matter by cooks and confectioners. If the heat is continued beyond 420° F., complete decomposition ensues, inflammable gases are given off and a brilliant mass of porous charcoal remains.

1027. Cane-sugar is not rendered brown as grape-sugar is (882) on boiling it in a solution of potash.

1028. "Concentrated sulphuric acts very energetically upon cane-sugar, evolving water, carbonic and formic acids and charcoal. It is a striking experiment to mix about equal bulks of oil of vitriol and strong syrup; the mixture, when stirred, becomes brown and black, then suddenly heats, boils up, and passes into the state of a bulky black magma:* the acid appears suddenly to abstract the elements of water from the sugar, leaving charcoal." The action of sulphuric acid upon grape-sugar is, as we have already noticed (879), very different.

1029. Strong nitric acid converts cane and grape-sugar into oxalic acid.

1030. When cane-sugar is boiled with dilute hydrochloric or sulphuric acid it assimilates water and becomes converted into grape-sugar. Yeast effects the same change in its solutions. The converse change, that of converting grape-sugar into cane, has not yet been accomplished.

1031. A sugar solution has the property of dissolving many basic oxides, baryta and lime are very soluble in cold sugar solutions; when the solution of the alkaline earth is heated, it becomes opaque, and when the solution reaches the boiling point the compound of sugar and the alkaline earth is deposited.

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* Cane sugar has been given as a test for free sulphuric acid in the presence of a sulphate (see par. 476).

1032. If to a solution of cane-sugar a solution of caustic potash is added, and then a drop or two of a dilute solution of sulphate of copper, a deep blue liquid is obtained, which retains its *blue tint*, on being heated. This is a very good test for distinguishing the two varieties of sugar, or discovering an admixture of grape with cane-sugar (see par. 882).

1033. The properties of grape-sugar have already been described under animal chemistry, see page 283.

ORGANIC BASES.

1034. In this section the deportment of the most important of the medicinal alkaloids with reagents is described, together with Sonnenschein's method for the detection and separation of the organic bases from mixtures of other substances.

1035. *Sonnenschein's method.*—" This method is founded upon the property which the alkaloids possess, in common with ammonia, of giving precipitates in an acid solution of *phosphomolybdate of soda;* it is very easy of execution, and seems to give very accurate results.

1036. " Phosphomolybdate of sodium is thus prepared. The yellow precipitate obtained by mixing acid solutions of molybdate of ammonia, and phosphate of soda is well washed, suspended in water, and heated with carbonate of soda till it is completely dissolved. The solution is evaporated to dryness, and the residue ignited till all ammonia is expelled; if any reduction of molybdic acid take place during the ignition, the product is moistened with nitric acid and again ignited. It is then heated with water, nitric acid added till the solution has a strongly acid reaction, and the gold-yellow solution thus obtained is diluted till 10 parts of the solution contain 1 part of solid residue. It must be carefully preserved from contact with ammonia.

1037. "This reagent is applied to the separation of the alkaloids in the following manner:—The whole of the organic matter to be examined is repeatedly exhausted with very dilute hydrochloric acid; the extract is evaporated at a heat of 86° F. to the consistence of a thin syrup, then diluted, and left for some hours in a cool place before filtration. The filtrate is precipitated by excess of phosphomolybdic acid, the precipitate collected on a filter, thoroughly washed with water containing phosphomolybdic and nitric acid, and introduced while moist into a flask. Caustic baryta is added to a distinct alkaline reaction; and the flask having been fitted with a delivery tube which is connected with a bulb apparatus containing hydrochloric acid, heat is gradually applied, when the ammonia and volatile organic bases distil over and are collected in the hydrochloric acid. The residue in the flask (containing the non-volatile alkaloids) is freed from excess of baryta by a current of carbonic acid, carefully evaporated to dryness on a water-bath, and extracted with strong alcohol. On evaporating the alcoholic solution, the bases are commonly obtained in a state of such purity that they will at once exhibit their characteristic reactions; occasionally, however, they require to be further purified by recrystallization from alcohol or ether."
—*Watts's 'Dictionary of Chemistry.'*

VOLATILE ALKALOID.

NICOTINA OR NICOTINE ($C_{20}H_{14}N_2$).

1038. Nicotine, in its pure state, is a limpid, colourless, oily liquid; it absorbs oxygen on exposure to air, and turns brown and finally becomes solid. It has a strong and irritating odour of tobacco; and is very inflammable and burns with a smoky flame. It is miscible in all proportions with water, alcohol, and ether. It boils at 482° F., suffering however partial decomposition in the process; but when heated in a stream of hydrogen gas, it distils over unaltered, between 212° and 392° F. Its solutions possess an alkaline reaction. It precipitates metallic oxides from solutions of their salts, and unites with the acids, forming salts.

1039. Salts of nicotine are in general very soluble in water and alcohol, but insoluble in ether; they are difficultly crystallizable and even deliquescent.

1040. If an aqueous solution of nicotine, or a solution of a salt of nicotine mixed with a solution of soda or potash, is shaken with *ether*, the nicotine is dissolved by the ether; if the latter is then allowed to evaporate on a watch-glass, the nicotine remains behind in drops and streaks; on warming the watch-glass, it volatilizes in white fumes of strong odour.

1041. *Chlorine* acts powerfully upon nicotine, producing with it a blood-red liquid.

1042. Solution of *iodine* in iodide of potassium and water, when added in small quantity to an aqueous solution of nicotine, produces a yellow precipitate, which after a time disappears. Upon a further addition of the iodine solution, a copious kermes-coloured precipitate separates; but this also disappears again after a time.

1043. When a glass rod moistened with *hydrochloric acid* is brought into contact with vapour of nicotine white fumes are produced, as with ammonia. Boiled with *hydrochloric acid*, the nicotine is coloured violet.

1044. When *nitric acid* is heated with nicotine a red liquor is produced.

1045. *Bichloride of platinum* produces in aqueous solutions of the chloride of nicotine a yellow crystalline precipitate of chloro-platinate of nicotine, which is insoluble in alcohol and ether, slightly soluble in cold water, readily soluble in an excess of nicotine, and soluble in hydrochloric acid in the cold.

1046. "*Terchloride of gold* produces a reddish-yellow flocculent precipitate, sparingly soluble in hydrochloric acid.

1047. "If an aqueous solution of nicotine is added to a solution of chloride of mercury in excess, an abundant, flocculent, white precipitate is formed. If solution of chloride of ammonium is now added to the mixture in sufficient quantity, the entire precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy white precipitate.

1048. "Solution of *tannic acid* produces a copious white precipitate, which redissolves upon addition of hydrochloric acid."

1049. Nicotine is extremely poisonous, a single drop of it being sufficient to kill a large dog. It is contained in tobacco, probably in the state of malate and citrate.

NON-VOLATILE ALKALOIDS.

1050. The non-volatile alkaloids are solid, and cannot be distilled over with water.

MORPHIA or MORPHINE ($C_{34}H_{19}NO_6$, 2Aq).

1051. Morphine when crystallized from alcohol, forms small but very brilliant prismatic crystals, which are transparent and colourless, it crystallizes with two equivalents of water; at a gentle heat the water is expelled and the morphine melts and forms a tumid resinous mass which solidifies into a radiated crystalline mass. When it is obtained by precipitation it appears as a white crystalline mass. It is soluble in about 1000 times its weight of cold and in 400 of boiling water; the solution has a bitter taste. It is soluble in about 90 times its weight of cold, and from 20 to 30 parts of boiling alcohol. Its aqueous and alcoholic solutions manifest distinctly alkaline reactions. It is nearly insoluble in ether.

1052. Acids dissolve morphine, forming with it salts which are most of them crystallizable. They are readily soluble in water and alcohol, but insoluble in ether. Its salts are exceedingly bitter to the taste.

1053. The fixed alkalies and ammonia precipitate morphine from the solution of its salts, an excess of the precipitant redissolves the precipitate. The precipitated morphine redissolves with great readiness in the fixed alkalies, but much less readily in ammonia. Lime water behaves like the fixed alkalies.

1054. The fixed alkaline carbonates precipitate morphine from the solution of its salts, and it does not redissolve in an excess of the precipitant. The fixed alkaline bicarbonates also precipitate it, and an excess does not redissolve the precipitate; these reagents fail to precipitate morphine from acid solutions in the cold.

1055. Precipitated morphine dissolves in chloride of ammonium, and with difficulty in carbonate of ammonia.

1056. If a neutral and concentrated solution of a persalt of iron be added to neutral and concentrated solutions of salts of morphine, a beautiful dark-blue colour is produced, which is characteristic of morphine. The colour disappears by an excess of acid, by the action of heat, and even by the addition of alcohol. If the solution contains an admixture of animal or vegetable extractive matters or of acetates, the colour will appear clouded or less distinct.

1057. Concentrated *nitric acid* colours morphine or its salts in the solid state, and also their *concentrated* solutions orange red, which passes by degrees to yellow.

1058. "If morphine or a compound of morphine is treated with pure concentrated *sulphuric acid*, and heat applied, a colourless solution is obtained; if after cooling, 8 to 20 drops of *sulphuric acid mixed with nitric acid** are added, and 2 or 3 drops of water, the fluid acquires a violet-red coloration (gentle heating promotes the reaction); and if a fragment of *binoxide of manganese* or of *chromate of potash* is then added, the fluid acquires an intensely mahogany-brown colour."—*Otto.*

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* "Mix 6 drops of nitric acid of 1·25 sp. gr. with 100 cubic centimètres of water, and add 10 drops of this mixture to 20 grammes of pure concentrated sulphuric acid."

1059. Morphine is contained in opium associated with narcotine and many other bases; see par. 1066.

NARCOTINA OR NARCOTINE ($C_{46}H_{25}NO_{14}+Aq$).*

1060. Narcotine appears in the form of acicular groups, or in colourless, brilliant, right rhombic prisms, or when precipitated by the alkalies, as a white, loose, crystalline powder. It fuses at 340° F., and loses one equivalent of water. It is insoluble in cold water, but dissolves in boiling water to the extent of 1 part in 7000. It dissolves sparingly in alcohol and ether in the cold, but somewhat more readily upon heating. Solid narcotine is tasteless, but the alcoholic and etherial solutions are intensely bitter. Its solutions do not possess an alkaline reaction.

1061. Narcotine dissolves readily in acids, forming with them salts; but the basic powers of narcotine are so feeble that its salts have invariably an acid reaction. "Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even by simple evaporation. Most of the salts of narcotine are amorphous, and soluble in water, alcohol and ether; they have a bitter taste."

1062. Pure alkalies, and alkaline carbonates and bicarbonates, precipitate narcotine immediately from a solution of its salts, in the form of a white powder, which, seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitant. If a solution of narcotine is mixed with ammonia, and ether added in sufficient quantity, the narcotine which has separated upon the addition of the ammonia redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the etherial solution is evaporated on a watch-glass, the residue is seen, upon inspection through a lens magnifying a hundred times, to consist of small, distinct, elongated, and lance-shaped crystals.

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* This is the formula assigned to narcotine by Blyth and Wholer; Matthiessen and Foster have more recently investigated it, and they assign it the formula $C_{44}H_{23}NO_{14}$.

1063. "*Concentrated nitric acid* dissolves narcotine to a colourless fluid, which acquires a pure yellow tint upon the application of heat.

1064. "If the solution of a salt of narcotine is mixed with *chlorine-water*, it acquires a yellow colour, slightly inclining to green; if ammonia is then added, a much more intensely coloured yellowish-red fluid is obtained.

1065. " If a small quantity of pure narcotine is treated with from 4 to 6 drops of pure *concentrated sulphuric acid*, no coloration is observed, not even on the application of a gentle heat, or at least, the heated fluid acquires only a barely perceptible yellow tint, but upon adding now, after cooling, from 8 to 20 drops of sulphuric acid mixed with a little *nitric acid*, (see foot-note, page 324), and 2 or 3 drops of water, the fluid acquires an intense red colour. Addition of binoxide of manganese does not materially change the colour."

1066. Opium contains besides morphine and narcotine, the following crystallizable alkaloids; *codeine*, *thebaine*, *narceine*, and *papaverine*. The following table shows the difference in the solubility of these alkalies in different liquids:

	Water.	Alcohol.	Ether.	Potash.
Morphine . .	Slightly soluble	Easily soluble	Almost insoluble	Soluble in an excess.
Narcotine . .	Almost insoluble	Soluble	Soluble	Insoluble.
Narceine . .	Slightly soluble	Soluble	Insoluble	Soluble in weak potash.
Codeine . . .	Soluble	Extremely soluble	Extremely soluble	Insoluble in concentrated potash.
Thebaine . .	Insoluble	Soluble	Soluble	Soluble in weak potash.
Papaverine . .	Insoluble	Soluble	Soluble	Insoluble.

QUINA OR QUININE ($C_{40}H_{24}N_2O_4+6Aq$).

1067. Quinine appears either in the form of silky needles, or as a loose white powder. It melts at 248° F., and gives up its water of crystallization. It is sparingly soluble in cold, but somewhat more readily soluble in hot water; it requires about 350 parts of water for its solution. It is readily soluble in alcohol both hot and cold, it is less soluble in ether. It is also soluble in the essential and fixed oils. Its solutions have an alkaline reaction and are intensely bitter.

1068. Acids dissolve quinine, forming with it salts which are crystallizable, and difficultly soluble in cold, but readily soluble in hot water and in spirit of wine. The acid salts dissolve very freely in water; the solutions exhibit the remarkable phenomenon of *fluorescence* or *epipolic dispersion*—a magnificent blue luminosity seen upon the surface of the liquid when viewed in reflected light, and which is owing to a change effected in the *actinic* rays by the dissolved quinine salt. If a cone of light is thrown into these solutions by means of a lens, either horizontally or vertically, a blue cone of light is seen even in highly dilute solutions. The salts of this base are intensely bitter.

1069. The fixed alkalies, ammonia, and the alkaline carbonates precipitate quinine from a solution of its salts in an amorphous state, which after some time becomes crystalline. The precipitate is only soluble in the fixed alkalies to a barely perceptible extent; but it is more soluble in ammonia. In the solutions of the fixed alkaline carbonates, it dissolves to about the same extent as in pure water.

1070. "The addition of *chlorine-water* to the solution of a salt of quinine fails to impart a colour to the fluid, or at least imparts to it only a very faint tint; but if ammonia is now added, the fluid acquires an intense emerald-green colour. If, after the addition of the chlorine water, some solution of *ferrocyanide of potassium* is added, then a few drops of *ammonia* or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. This reaction is delicate and characteristic. Upon addition of an acid (acetic acid answers the purpose best) to the red fluid, the colour vanishes, but reappears afterwards upon cautious addition of ammonia.

1071. If a solution of quinine is mixed with ammonia, ether added, and the mixture shaken, the quinine which has separated upon the addition of the ammonia, redissolves in the ether. In this respect quinine differs essentially from cinchonine, and the two bases can be readily separated and detected in the presence of each other; for if they are both present the quinine is dissolved in the ether, whilst the cinchonine remains in suspension on the surface of the aqueous stratum.

CINCHONIA, OR CINCHONINE ($C_{40}H_{24}N_2O_2$).

1072. Cinchonine appears either in the form of transparent brilliant, four-sided prisms, or fine, white, crystalline needles, or, if precipitated from concentrated solutions, as a loose white powder; in its crystalline state, it is anhydrous. It is nearly insoluble in cold, and dissolves only with extreme difficulty in hot water. It is less soluble in alcohol than quinine, and is more soluble in hot than cold alcohol. The greater portion of the cinchonine dissolved by hot alcohol, separates in a crystalline form as the solution cools. It is insoluble in ether. Solutions of cinchonine have an alkaline reaction and a bitter taste. It fuses at 329° F., to a colourless liquid, which becomes a crystalline mass on cooling.

1073. The acids dissolve cinchonine, forming with it salts which are most of them crystallizable, they are soluble in water and alcohol; insoluble in ether. They are exceedingly bitter to the taste.

1074. The fixed alkalies, ammonia, and the neutral alkaline carbonates precipitate cinchonine from a solution of its salts, in an amorphous state, an excess of the precipitant does not redissolve the precipitate.

1075. "If the solution of a salt of cinchonine containing only very little or no free acid, is mixed with ferrocyanide of potassium, a flocculent precipitate of ferrocyanide of cinchonine is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but separates again upon cooling, in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic."

STRYCHNIA OR STRYCHNINE ($C_{42}H_{22}N_2O_4$).

1076. Strychnine crystallizes from dilute alcohol, in white anhydrous octohedra, or in square prisms, which do not fuse on the application of heat; when it is produced by precipitation or rapid evaporation, it appears as a white powder. It does not fuse when heated. Cold water does not dissolve more of it than $\frac{1}{7000}$th of its weight, and it is only slightly more soluble in hot water. It is only sparingly soluble in dilute alcohol, and almost insoluble in absolute alcohol and ether. It dissolves freely in amyl-alcohol, and is soluble in chloroform and the essential oils. It is very bitter to the taste; even when its cold aqueous solution is diluted with 100 times its weight of water, it still possesses a distinctly bitter taste.

1077. Acids dissolve strychnine, forming with it salts, most of which are crystallizable; they are soluble in water, and are very bitter to the taste.

1078. The fixed alkalies and their carbonates precipitate strychnine from solutions of its salts. The precipitate is insoluble in an excess of these reagents; and the strychnine is only precipitated after the lapse of some time from dilute solutions.

1079. Ammonia precipitates strychnine from a solution of its salts, but the precipitate is soluble in an excess of the ammonia; from which solution the strychnine separates after some time, in the form of needles; the length of time required for the separation depending upon the strength of the solution.

1080. If strychnine is dissolved in a drop or two of *pure concentrated* sulphuric acid, no coloration is produced, but if a very small quantity of some oxidizing agent (chromate of potash or permanganate of potash is the best) in the solid form is added, the fluid acquires a magnificent blue-violet colour, which after some time, changes to wine red, then reddish yellow. "Metallic chlorides and considerable quantities of nitrates, also large quantities of organic substances, prevent the manifestion of the reaction or impair its delicacy. It is, therefore, always advisable to free the strychnine first, as far as practicable, from all foreign matters before proceeding to try this reaction."

1081. Concentrated nitric acid dissolves strychnine, forming a solution colourless in the cold, but which becomes slightly yellow on heating. If to this solution a small quantity of peroxide of lead be added, the same changes of colour may be witnessed as in the preceding experiment. These and similar colour experiments ought to be performed on a piece of white porcelain.

1082. "Strychnine is associated in nature with the next base, brucine, which may be readily distinguished from it by being soluble in absolute alcohol. The action, too, of nitric acid upon the two bodies differs; it dissolves brucine, and colours the solution intensely red; when heated, this colour changes to yellow; and if protochloride of tin, or sulphide of ammonium be then added, the colour again changes and becomes a most intense violet."

BRUCIA OR BRUCINE ($C_{46}H_{26}N_2O_8 + 8Aq$).

1083. Brucine appears either in the form of transparent straight rhombic prisms, or in that of crystalline needles aggregated into stars, or as a white powder composed of minute crystalline scales. It melts readily on the application of heat, and loses its water of crystallization. It is easily distinguished from strychnine, which it resembles in many respects, by its ready solubility, both in dilute and absolute alcohol. It is difficultly soluble in cold, but somewhat more soluble in hot water; one part dissolving in about 500 parts of hot water. It is soluble in amyl-alcohol. It is insoluble in ether. Its taste is intensely bitter.

1084. The acids dissolve brucine, forming salts, most of which are crystallizable; they are readily soluble in water, and are very bitter to the taste.

1085. The fixed alkalies and their carbonates precipitate brucine from a solution of its salts, the precipitate is not soluble in an excess of these reagents. "Viewed under the microscope immediately after precipitation it appears to consist of very minute grains; but upon further inspection these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves, without exception, into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye."

1086. Ammonia precipitates brucine from its solutions; the precipitate appears at first in the form of minute drops of oil, but which finally change to white needles. The precipitate is very soluble in an excess of ammonia; but it is deposited after a time, the length of time depending upon the strength of the solution, from the ammoniacal solution in a crystalline state.

1087. The nitric acid reaction described in par. 1082 is characteristic for brucine.

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